GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF RESEARCH ADMINISTRATION

Date: 28 May 1970

RESEARCH PROJECT INITIATION

Project Title: Chemistry of Carbanions

Project No.: B-1580

Project Director: Dr. Erling Grovenstein, Jr.

Sponsor: National Science Foundation

Agreement Period: From 1 May 1970 until 30 April 1972

Type Agreement: Grant No. GP-19251 (Renewal of GP-8309)

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$40,000 NSF Funds (B-1580)
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$50,185 Total Budget

Grant Administrator

Dr. Donald A. Speer
Program Director
Chemical Dynamics Program
National Science Foundation
Washington, D.C. 20550

Reports Required

Annual - 1 May 1971

Final - Upon completion of project

Note: Continuation of B-1530

300. B-1580 (Sch)

Assigned to: School of Chemistry

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Other File B-1580

RA-3 (4/65)

GEORGIA INSTITUTE OF TECHNOLOGY

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RESEARCH PROJECT TERMINATION

Date: 22 January 1973

Project Title "Chemistry of Carbanions"

Project No: G-33-620 (formerly B-1582)

Principal Investigator: Dr. E. Grovenstein

Sponsor: National Science Foundation

Effective Termination Date: 31 October 1972

Clearance of Accounting Charges: All charges have cleared.

Grant/Contract Closeout Actions Remaining:

All grant requirements have been met.

NOTE: Research continued under Project G-33-648

Assigned to: School of Chemistry

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RA-4 (6-71)

G-33620

Resumé of Progress to Date upon "Chemistry of Carbanions"

For Period May 1, 1970-September 30, 1971

NSF Grant No. GP-19251

by Erling Grovenstein, Jr., Principal Investigator

PART I. Studies upon Rearrangements of Carbanions

Since comparatively few cases of rearrangement of carbanions are known at present, most of our efforts have been directed toward learning the structural features and reaction conditions necessary for rearrangement. We report here the first successful example of [1,2] anionic sigmatripic rearrangement[1] of an aryl group attached to a secondary carbon atom, the first examples of [1,4] and [1,5] rearrangement of phenyl and of [1,4] rearrangement of p-biphenylyl, the second example of [1,2] and/or [3,2] sigmatropic rearrangement of an allylic group in an anion containing only carbon and hydrogen, and apparent examples of [1,2] and [1,4] anionic rearrangements of hydrogen. Finally we report in a [1,4] rearrangement of p-biphenylyl the identification by spectroscopic and chemical methods of a fairly stable, novel spiro anion which corresponds in general structure to the type of intermediate long suspected (but never isolable) in [1,2] sigmatropic anionic rearrangements of aryl groups.

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(1) For the definition, theory, and examples of sigmatropic rearrangements, see R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, GmbH, Weinheim, 1971, pp. 114-140.

A. [1,2] Rearrangement of p-Biphenylyl in 2-p-Biphenylylethyl Anion[2]

While [1,2] anionic sigmatropic rearrangements of phenyl and other aryl groups are known,[3] rearrangements in appreciable quantity to date have always involved aryl migration from a quaternary carbon attached to at least one aryl group (or other unsaturated groups[4]) such that the product of migration is normally more stable and is less sterically compressed than the starting organoalkali compound. Cram and Dalton[5] have reported that threo-2-phenyl-3-pentyl methanesulfonate with potassium in 1,2-dimethoxyethane at 25° gave 94.5% of 2-phenylpentane and 5.5% of 3-phenylpentane (product of phenyl migration from a tertiary carbon); threo-3-phenyl-2-pentyl methanesulfonate with sodium in liquid ammonia gave 75% of 3-phenylpentane and 3% of 2-phenylpentane; and 1,1-dideuterio-1-methoxy-2-(1-naphthyl)-ethane and 1,1-dideuterio-2-(1-naphthyl)-ethyl methanesulfonate with potassium in 1,2-dimethoxyethane at 0° gave 1-ethylnaphthalene deuterated only in the methyl group [no detectable rearrangement (less than 5%) accompanied reduction].

In order to test to see if [1,2] sigmatropic anionic rearrangements are restricted to migrations from a quaternary carbon bearing one or more

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(2) This work was reported in part at the XXIII International Congress of Pure and Applied Chemistry, Boston, Mass., July, 1971, p. 112 of Abstracts.

(3) E. Grovenstein, Jr., and co-workers, J. Amer. Chem. Soc., 79, 4985 (1957); ibid., 83, 412 (1961); ibid., 89, 1852 and 2348 (1967). H. E. Zimmerman and co-workers, ibid., 79, 5455 (1957); ibid., 83, 1196 (1961).

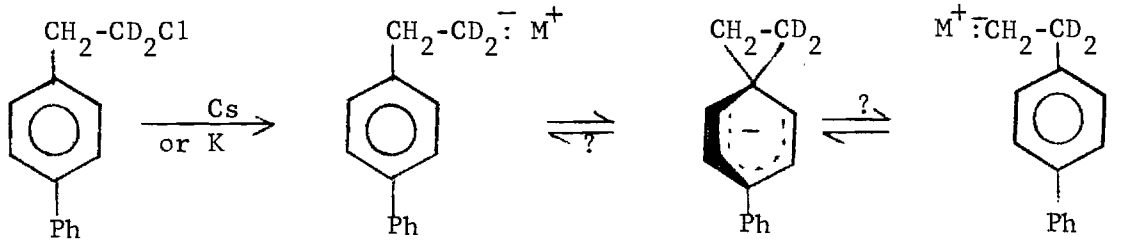
(4) S. W. Staley and J. P. Erdmon, J. Amer. Chem. Soc., 92, 3832 (1970).

(5) D. J. Cram and C. K. Dalton, ibid., 85, 1268 (1963).

unsaturated groups, 1-chloro-2-p-biphenylylethane-1,1-$\underline{d}_2$ has been synthesized and allowed to react with alkali metals under a variety of conditions. With lithium metal in tetrahydrofuran (THF) at -70° this halide gave 2-p-biphenylylethyllithium-1,1-$\underline{d}_2$ containing less than 5% of the rearrangement product 2-p-biphenylylethyllithium-2,2-$\underline{d}_2$ according to nmr analysis of the carboxylic acid obtained on carbonation. When 2-p-biphenylylethyllithium-1,1-$\underline{d}_2$ (prepared at -70°) is held at 1 ± 1° for 9 hours, the final organolithium compound has only some 8% 2-p-biphenylylethyllithium-2,2-$\underline{d}_2$. Attempts to increase the extent of rearrangement by increasing the time resulted (at 2 ± 1° for 16.5 hr) in negligible organolithium compound but dominant 1-p-biphenylylethane-2,2-$\underline{d}_2$ containing only 2% of 1-p-biphenylethane-1,1-$\underline{d}_2$. Attempts to increase the extent of rearrangement at 4° by addition of N,N,N′,N′-tetramethylethylenediamine were also unsuccessful. In conclusion 1-chloro-2-p-biphenylylethane-1,1-$\underline{d}_2$ reacted with lithium at -70° to give essentially pure 2-p-biphenylylethyllithium-1,1-$\underline{d}_2$ which failed to rearrange appreciably (< 10%) under any of the conditions tested.

Reaction of 1-chloro-2-p-biphenylylethane-1,1-$\underline{d}_2$ with Cs-K-Na alloy in THF at -65° gave predominantly p-biphenylylethane which contained 9% and, in a separate run, 22% of product of [1,2] p-biphenylyl rearrangement. Reaction with cesium in THF at 65° gave a product which consisted essentially of a 50/50 mixture of p-biphenylylethane-2,2$\underline{d}_2$ and -1,1-$\underline{d}_2$; a similar result was obtained with potassium in THF at 65°. Thus it is concluded that in reaction with cesium and potassium in refluxing THF, the two methylene groups become equibrated, likely by way of a symmetrical intermediate such as II (see Scheme I):

Scheme I:



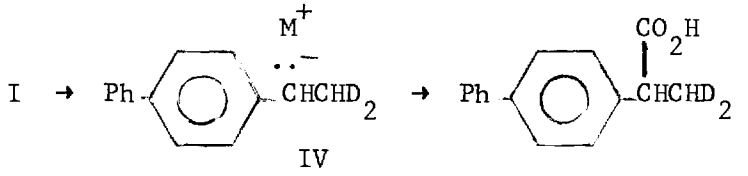
I II III

A number of questions immediately arise concerning the validity of Scheme II. Does cyclization occur in an anion or a free radical? Is cyclization concerted such that intermediate I is not really formed? To help answer these questions the reaction of 1-chloro-2-p-biphenylyl-1,1-d_2 with potassium was carried out in refluxing THF having a little t-butyl alcohol and, in a second very similar experiment t-BuOD. Mass spectroscopic and nmr analyses of the p-biphenylylethane produced, showed that less than 19% rearrangement of p-biphenylyl occurred in presence of t-butyl alcohol. t-Butyl alcohol should be less effective in trapping alkyl free radicals than tetrahydrofuran[6] but much more effective in protonation of carbanions, consequently we conclude that, since addition of t-butyl alcohol nearly stops the rearrangement, essentially all of the 2-p-biphenylethyl must exist as an anion (doubtlessly as I) prior to cyclization. We believe, therefore, that it is the anion I which undergoes cyclization to II.

The present results do not require that the cyclic anion II undergoes ring opening to give I and III, however attractive this may seem. Indeed in one experiment with cesium in THF at reflux, a by-product 2-p-biphenylylpropanoic acid-3,3-d_2 was obtained (in 6% yield) whose isotopic labeling indicates that it could not have come from II, an equilibrium mixture of

(6) Cf. W. A. Pryor, Chem. & Eng. News, June 7, pp 42-43 (1971).

I and III, or from the 50/50 mixture of isotopically labeled p-biphenylylethanes which were isolated from the run. The most likely interpretation is that the 2-p-biphenylylpropanoic acid-3,3-d_2 came from carbanion I by way of IV



If this interpretation is correct, then the p-biphenylylethane which was isolated evidently came from protonation of the cyclic intermediate II. This conclusion needs to be verified.

In conclusion the ready migration of p-biphenylyl in 2-p-biphenylylethylpotassium and -cesium constitutes the first example[7] of a [1,2] anionic sigmatropic rearrangement of an aryl group attached to a secondary carbon atom. Cram and Dalton's lack of success[5] in the 1-naphthyl system may be due to the more acidic character of the solvent (1,2-dimethoxyethane) which they used.

B. [1,4] and [1,5] Rearrangement of Phenyl in 4,4,4-Triphenylbutyl and 5,5,5-Triphenylamyl Anions

With potassium metal in THF at reflux temperature, 4-chloro-1,1,1-triphenylbutane gives chiefly 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene; with Cs-K alloy at -49°, the initial product is 1,1,1-triphenylbutane along with some 9% of 1,1,4-triphenylbutyl anion, the product of [1,4] phenyl migration. Reaction of 5-chloro-1,1,1-triphenylpentane with potassium or with

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(7) A full paper on this work is in process of preparation.

Cs-K and Cs-K-Na alloys in THF gives primarily 1,1,1-triphenylpentane as initial product along with (for cesium alloys) some 6% of a product of [1,5] migration of phenyl. These major findings were reported under our previous grant (NSF GP-8309). The chief new work in this area was to confirm and clarify[8] some of the unusual results (such as the differences between potassium and the cesium alloys on the 4-chloro compound). A full paper describing this work has now been submitted for publication.

C. [1,4] Rearrangement of p-Biphenylyl in 4-Biphenylyl-4,4-diphenylbutyl Anion[2]

While [1,4] rearrangement of phenyl was obtained in the 4,4,4-triphenylbutyl system (see previous section), the amount of this rearrangement did not exceed 9% under the most favorable conditions studied. In order to learn more concerning the mechanism of such [1,4] rearrangements, a new system derived from 4-chloro-1-(p-biphenylyl)-1,1-diphenylbutane has been studied since, in view of the demonstrated[9] greater migratory aptitude of p-biphenylyl over m-biphenylyl and likely over phenyl, this system was expected to give more facile [1,4] rearrangement of p-biphenylyl than the previous system did of phenyl. This expectation has now been fully confirmed.

Reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane with lithium in THF at -70° gave upon hydrolysis a 76 to 24 ratio of 1-p-biphenylyl-1,1-diphenylbutane to 4-p-biphenylyl-1,1-diphenylbutane; upon standing for 4 hr at

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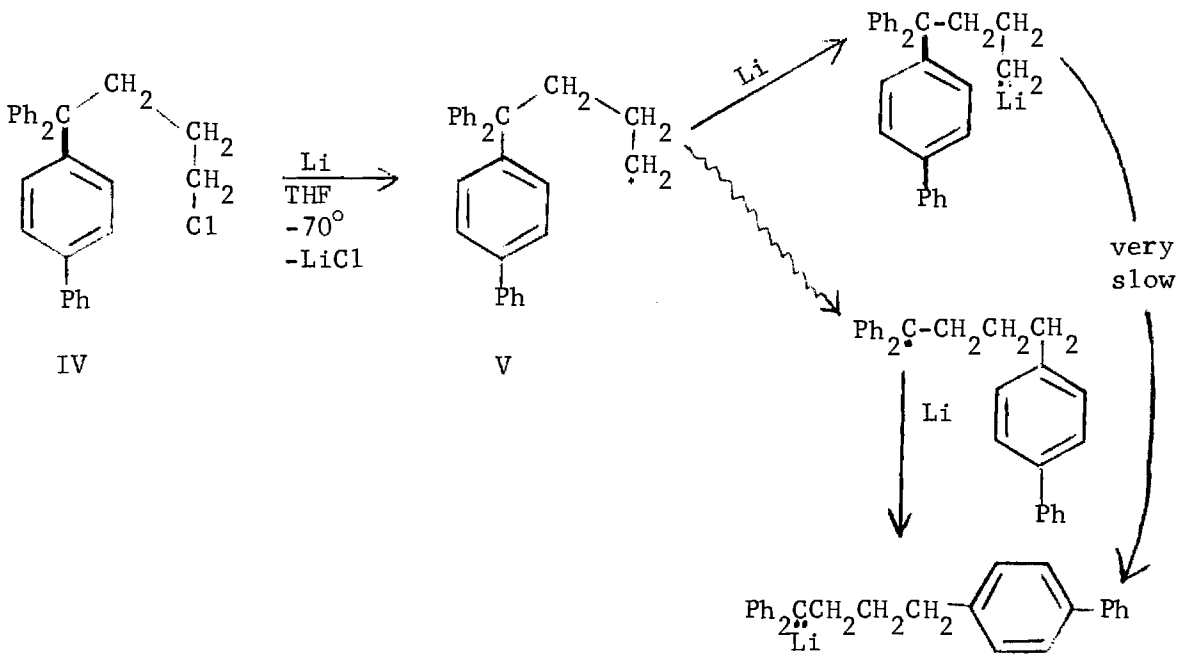
(8) Work of Mr. William B. Shannon, N.S.F. Undergraduate Science Summer Trainee, 1971.

(9) E. Grovenstein, Jr., and G. Wentworth, J. Amer. Chem. Soc., 89, 2348 (1967).

0°, the solution gave a 66 to 34 ratio of non-rearranged to rearranged products. Since 24% rearrangement took place during the reaction with lithium at -70° but only 10% more rearrangement at 0°, it is concluded that 4-p-biphenylyl-4,4-diphenylbutyllithium rearranges very slowly even at 0°; therefore the larger quantity of rearrangement at -70° must be via another process — we suggest that this is rearrangement[10] of an intermediate radical V (see Scheme II):

Scheme II:



Reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane with potassium or cesium in THF at 65° or with Cs-K-Na alloy in THF at -75° gives in each case, upon carbonation, a high yield of 5-p-biphenylyl-2,2-pentanoic acid. These results suggest that both 4-p-biphenylyl-4,4-diphenylbutylcesium and

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(10) See E. Grovenstein, Jr., and Y.-M. Cheng [Chem. Comm., 101 (1970)] for an analogous rearrangement during reaction of neophyl chloride with lithium.

-potassium undergo very ready [1,4] rearrangement of p-biphenylyl even at -75° (4 min reaction time); alternatively rearrangement could take place in the corresponding free redical V as observed with lithium metal. To distinguish between these possibilities the experiments summarized in Table I were performed. While the results are somewhat complicated by reduction of the biphenyl nucleus, this table shows that, whereas the chloride reacts with potassium in THF with essentially complete [1,4] rearrangement of the biphenylyl group, in presence of excess t-butyl alcohol rearrangement is completely blocked. With the less effective proton donor, triethylcarbinol, rearrangement is much more extensive; with the still less acidic n-butylamine, rearrangement is almost as complete as in pure tetrahydrofuran. Since the extent of rearrangement varies inversely with the proton donor ability of the reaction medium (not the hydrogen atom donor ability which was approximately constant in Exp. 1-5 of Table I), the results agree well with the idea that it is a carbanion (or organoalkali compound) which is undergoing rearrangement and which is trapped prior to rearrangement by addition of weak acids (see Scheme III).

Scheme III:

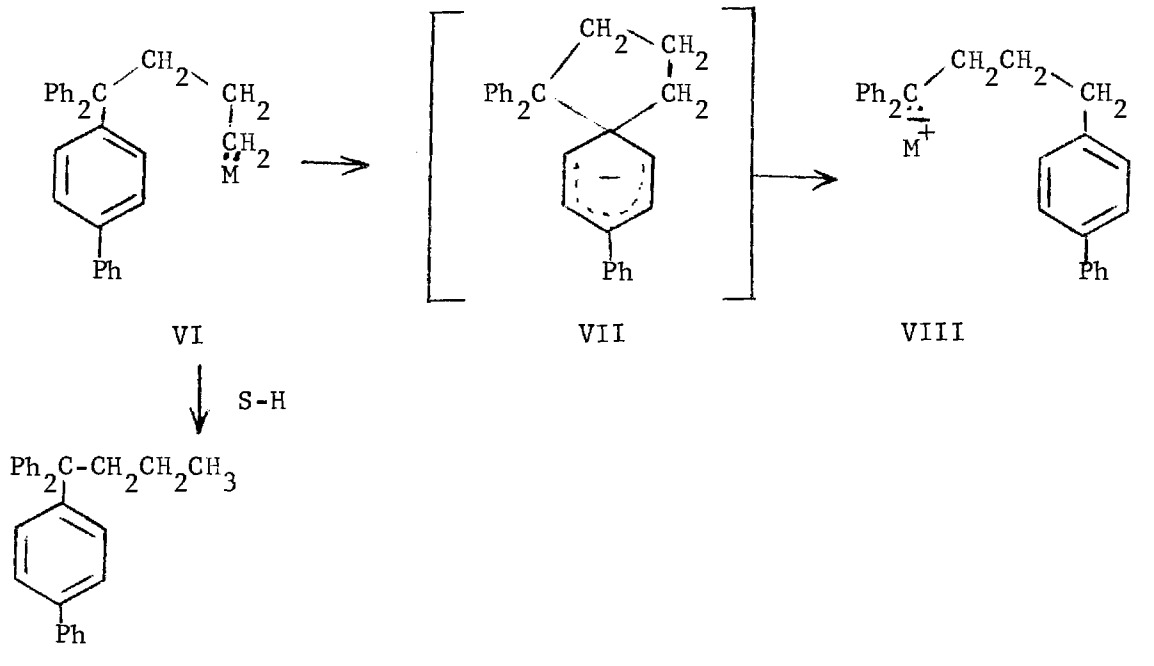
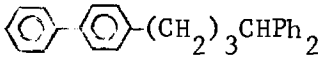
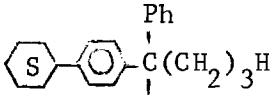
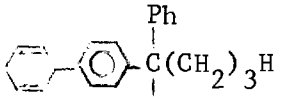
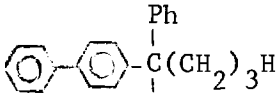


Table I. Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Alkali Metals in Various Media

Exp. No.	Conditions	Products, %			
					
(1)	React with K in THF at 65° and then add CH_3OH	97.6	0	0	1.4[a]
(2)	2.6 mmoles RCl with 5.8 mg-at. of K + 13 mmoles t-BuOH in THF at 65°	0	13.8	-	12.5[b]
(3)	The reaction mixture from (2) treated 7 times successively with 6 mg-at. of K and 6 mmoles t-BuOH at 65° in THF	0	90	5.8	3.4
(4)	2.3 mmoles RCl with 7.1 mg-at. of K and 6.8 mmoles of $(CH_3CH_2)_3COH$ at 65° in THF	52	0	8	7[c]
(5)	2.7 mmoles RCl with 5.8 mg-at. of K and 12.5 mmoles of n-$BuNH_2$ at 65° in THF and then addition of CH_3OH	95	0	0	4.5
(6)	React with Na in dioxane at 101°	8	0	0	92
(7)	React with K in dioxane at 101° and then addition of EtOH	75	0	0	0[d]

[a]There was also found 0.8% of $Ph_2CHCH_2CH_2CH_3$ and 0.2% of p-$PhC_6H_4CHPh_2$. [b]The remainder was unreacted RCl. [c]The remainder consisted of 25% of unreacted RCl and 9% of an unknown. [d]The remainder consisted of 12% of an unknown hydrocarbon and the rest non-volatile (glpc) material; carbonation of a portion gave 26% yield of a complex mixture of acids and 74% yield of the same volatile neutral products.

In Exp. 6 and 7 of Table I, the effect of change of solvent from tetrahydrofuran to dioxane and change of alkali metal from potassium to sodium is investigated. In both tetrahydrofuran and dioxane, potassium reacts with 4-chloro-1-p-biphenylyl-1,1-diphenylbutane to give almost exclusively products of [1,4] rearrangement of p-biphenylyl; in tetrahydrofuran at 65° the product is the corresponding 4-p-biphenylyl-1,1-diphenylbutyl anion whereas in dioxane it is predominantly the corresponding hydrocarbon. Evidently dioxane at 101° is more acidic (toward carbanions) than THF at 65° (although THF is a better hydrogen atom donor than dioxane[6]). In contrast to potassium, sodium metal in dioxane gives predominantly the non-rearranged hydrocarbon. Taken along with the earlier experiments with lithium and cesium, the present results show that the ease of [1,4] anionic rearrangement of p-biphenylyl increases along the series: RLi < RNa < RK ≃ RCs.

D. Cyclization of 4-p-Biphenylylbutyl Anion; Isolation of the Intermediate in [1,4] Rearrangement of p-Biphenylyl[11]

Both in the [1,2] and [1,4] rearrangements of phenyl and p-biphenylyl spirocyclic anionic intermediates have been postulated (see II in Scheme I and VII in Scheme III); however, no direct evidence for these transient intermediates has ever been obtained such that it is unclear whether structures such as II and VII correspond to transition states or reaction intermediates. Evidence in favor of the latter interpretation has now been obtained.

Reaction of 1-chloro-4-p-biphenylylbutane-1,1-d_2 with lithium metal in THF at -70° followed by carbonation gave a mixture of acids consisting

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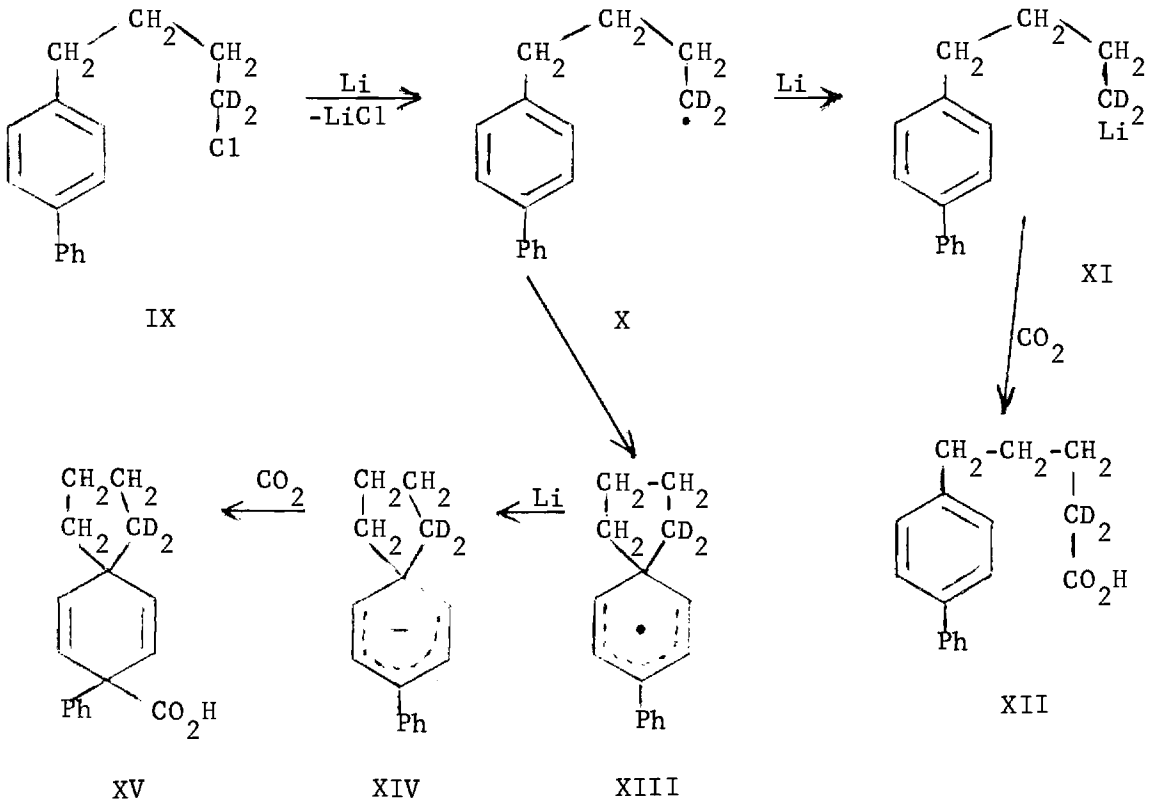
(11) This work (by Dr. S. Akabori) was partially supported by the present NSF grant but was primarily supported by funds supplied by the School of Chemistry, Georgia Institute of Technology.

of 65% of XII and 35% of XV (see Scheme IV). Since the straight chain acid XII was uniquely labeled with deuterium as shown, it is obvious that no symmetrical spiro intermediate such as XIV or XIII could have been its precursor. Since the yield of spiro products was not increased on warming the present mixture of organolithium compounds XI and XIV to 5°, it seems unlikely that XI can yield XIV at -70°. Hence it appears that the rearranged product XIV was formed via rearrangement of the radical X rather than by rearrangement of an organoalkali compound.

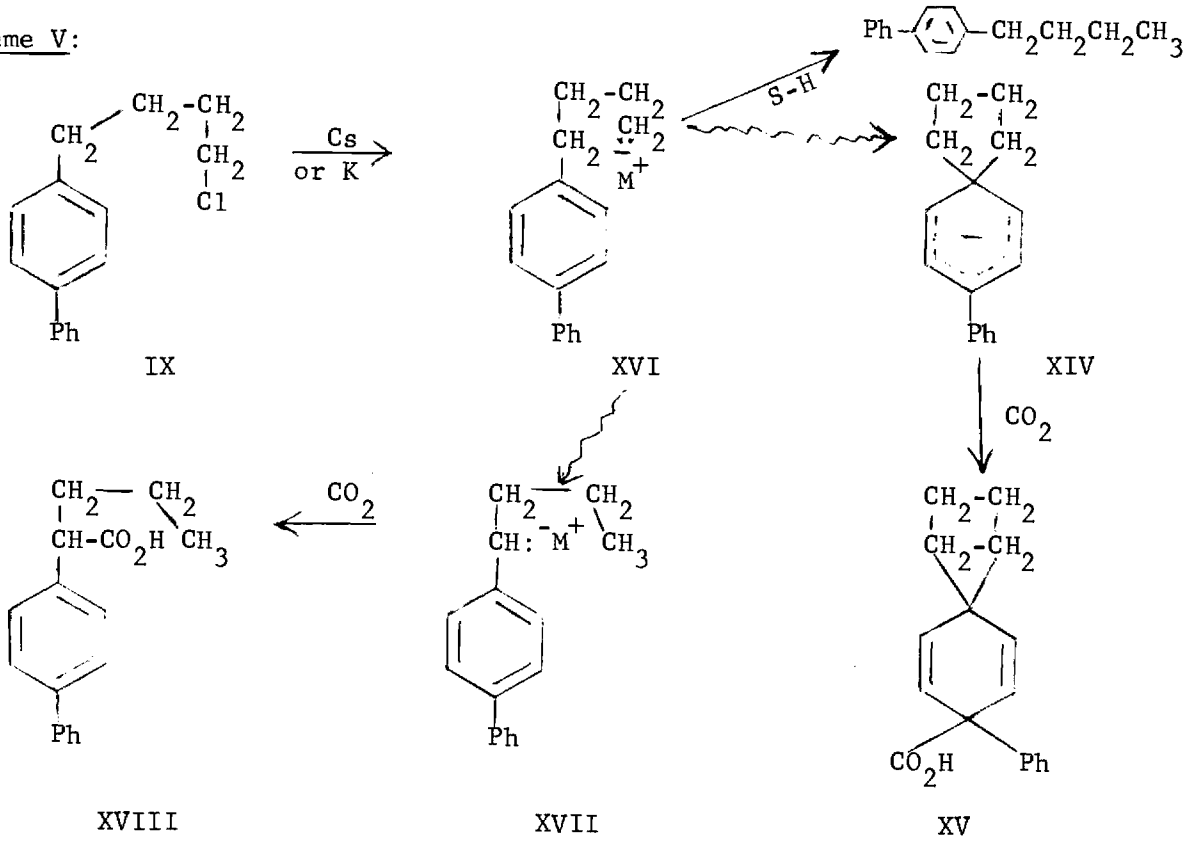
Scheme IV:



In contrast to lithium reaction of cesium and potassium with 1-chloro-4-p-biphenylylbutane in THF at 65° gave upon carbonation 80/20 and 76/24

ratios of acids XV/XVIII where XVIII appears to be 2-p-biphenylylpentanoic acid. Repetition of this reaction with excess Cs-K-Na alloy at -70° gave a 96% yield of acids in which the ratio of XV to XVIII was 97/3. Thus a nearly quantitative yield of spiro anion XIV has been obtained. The structure of this red anion which is reasonably stable in THF at room temperature has been confirmed by study of its nmr spectrum in perdeuterio-tetrahydrofuran. Since 1-chloro-4-p-biphenylylbutane-1,1-d_2 reacts with sodium in dioxane at 101° to give only 1-p-biphenylylbutane-4,4-d_2, evidently reaction with sodium gives first the 4-p-biphenylylbutyl anion XVI which is subsequently protonated by solvent to give 1-p-biphenylylbutane prior to cyclization. Presumably reactions with Cs and K involve the same intermediate anion XVI which rearranges in large part to the spiro anion XIV and in part to the benzylic anion XVII (see Scheme V).

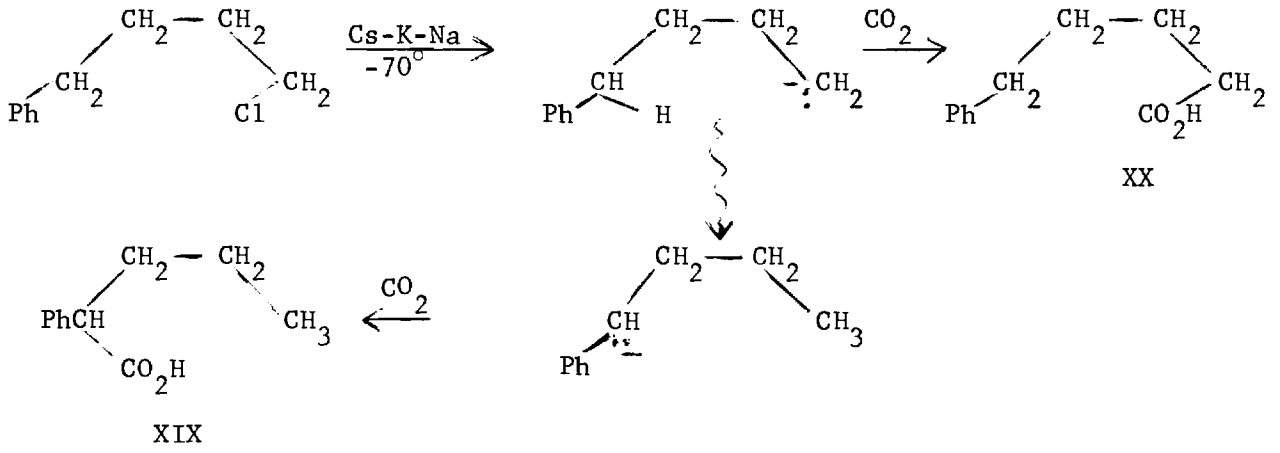
Scheme V:



E. [1,4] Rearrangement of Hydrogen in 4-Phenylbutyl Anion[11]

Addition of 1-chloro-4-phenylbutane to excess Cs-K-Na alloy at -70° in THF over a period of three minutes followed by stirring for one minute before carbonation gave 74% yield of acidic compounds. Analysis of these by glpc as methyl esters indicated that the acids contained 86% yield of 2-phenyl-1-pentanoic acid (XIX), 2.5% of 4-phenyl-1-pentanoic acid (XX), and small quantities of three unknowns. Thus in sharp contrast to the 4-p-biphenylylbutyl anion which primarily undergoes cyclization to XIV, the 4-phenylbutyl anion undergoes what appears to be a [1,4] rearrangement of hydrogen (see Scheme VI).

Scheme VI:



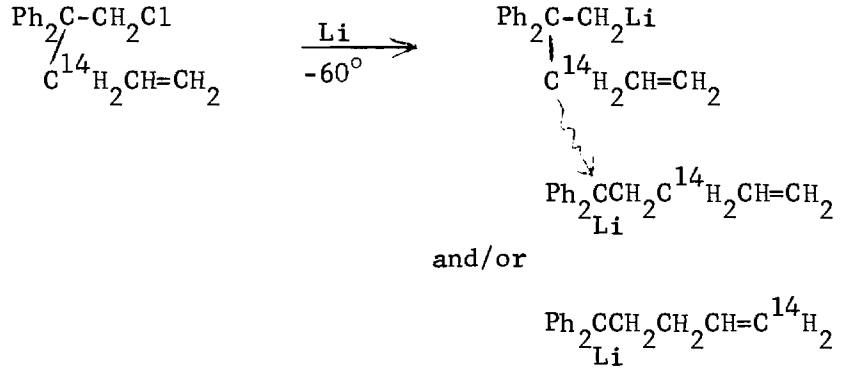
Under comparable conditions at -70° with 4-p-biphenylylbutyl anion only some 3% of [1,4] rearrangement of hydrogen occurred (see earlier discussion). We would emphasize the extreme rapidity of the present [1,4] rearrangement. We assume that the present rearrangement is intramolecular, but this remains to be established. As far as we are aware, a rearrangement of the present type across a saturated system has never been previously reported for carbanions.

In the realm of free radical reactions, [1,5] and, less commonly, [1,6] migrations of hydrogen from carbon to nitrogen have been reported in the Hofmann-Löffler reaction of N-haloamines in sulfuric acid solution. For an apparent example of [1,2] migration of a proton in 2-p-biphenylylethyl-1,1-d_2 anion see Section I A of this report.

F. [1,2] and/or [3,2] Rearrangement of Allyl in 2,2-Diphenyl-4-pentenyl Anion[12]

2,2-Diphenyl-4-pentenyllithium was prepared by reaction of the corresponding chloride with lithium in THF at -60°. Upon warming to 0° the lithium compound underwent rearrangement go give 1,1-diphenyl-4-pentenyllithium as deduced from the products of carbonation and protonation. Thus the allyl group has a greater migratory aptitude than a phenyl group in the present system. The present work is in process of repetition with one end of the allylic system labeled with carbon-14 in order to discover if this is a [1,2] and/or a [3,2] rearrangement of allyl (see Scheme VII).

Scheme VII:



(12) This work (by Mr. A. B. Cottinghem) was only partially supported by funds from the present NSF grant.

The present work provides the second example of migration of allyl in an anion containing only carbon and hydrogen and seems to offer advantages over the previous system,[13] especially in the use of carbon-14 rather than two methyl groups to label the ends of the allyl system.

PART II. Reactions of Cesium and Cs-K-Na Alloy with Aromatic Hydrocarbons

In view of the reluctance of benzene to add Na-K Alloy[14] to give an appreciable quantity of radical anion, it is surprising to read that cesium reacts with excess benzene to give a black precipitate. Hackspill[15] who first observed this reaction suggested that this precipitate was phenylcesium formed by the process:

$$3\ C_6H_6 + 2\ Cs \rightarrow 2\ C_6H_5Cs + C_6H_8$$

Later Hackspill[16] questioned the structure of this product and noted that the compound merited further attention. Subsequently de Postis,[17] working in Hackspill's laboratory, came to the conclusion that the black compound had the empirical formula of $C_6H_6Cs_6$ and was a loose addition compound of benzene with cesium, since it was attacked by water with evolution of hydrogen, did not react with gaseous CO_2, and failed to give "normal" alkylation products with alkyl halides. Other benzenoid compounds such as t-butylbenzene and,

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(13) For the first example, which was reported after our work was well underway, see J. E. Baldwin and F. J. Urban, Chem. Comm., 165 (1970).

(14) R. G. Kooser, W. V. Volland, and J. H. Freed, J. Chem. Phys., 50, 5243 (1969).

(15) L. Hackspill, Eighth International Congress of Applied Chemistry (New York), 2, 113 (1912); Ann. chim. et phys., [8], 28, 653 (1913).

(16) L. Hackspill, Helv. Chim. Acta, 11, 1026 (1928).

(17) J. de Postis, Eleventh International Congress of Pure and Applied Chemistry (London), 5, 867 (1947). See also L. Hackspill, "Nouveau Traité de Chimie Minerale," P. Pascal, 3, 125 (1956).

under certain conditions, cumene and diphenylmethane were reported[17] to form similar addition compounds with cesium. Since a cesium cation is about the same size as a benzene ring, it was suggested that steric factors prevented six cesium atoms from interacting strongly with a single benzene nucleus.

In the course of our work upon carbanion rearrangements, we have undertaken to prepare carbanions by interaction of cesium metal and Cs-K-Na alloy with arylalkyl chlorides. This work led to some unexpected results.[18] In light of this and the peculiar reports of Hackspill and de Postis, we have undertaken a rather extensive study of the interaction of cesium and Cs-K-Na alloy with aromatic hydrocarbons.

A. Benzene

In a preliminary investigation, we find that cesium reacts at 40° with excess benzene (the latter as reaction medium) to give a black precipitate which, after washing with isooctane, has about a one to one ratio of bound cesium to benzene (if unreacted cesium metal, as measured by hydrogen evolution on hydrolysis, is subtracted from the total cesium). Since the black product gives essentially no esr signal, it cannot be a radical anion. Reaction of the black precipitate with iodine gave a mixture in which 27% of the benzene rings were present as benzene and 73% were present as biphenyl. Hydrolysis of the black precipitate gave a product which contained 14% of the benzene rings as benzene, 15.5% as 1,4-dihydrobenzene, and the remainder as biphenyl, dihydrobiphenyl, tetrahydrobiphenyls, and a little phenylcyclo-

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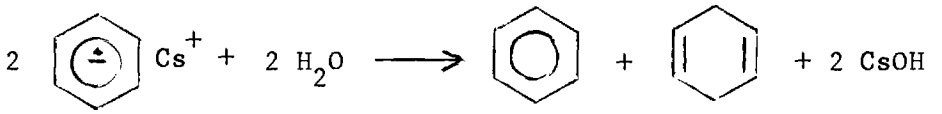
(18) Unpublished work with J. A. Beres, Y.-M. Cheng, and J. A. Pegolotti.

hexane. These products suggest that the black precipitate is in good part the di-cesium addition product of biphenyl.[19]

In a still more informative experiment, finely divided cesium was allowed to react with excess benzene in THF at -70°. The results are summarized in Table II. On the likely assumption that 1,4-dihydrobenzene is formed from a one-to-one adduct (cesium benzene) according to the overall stoichiometric equation,



it is seen that initially the yield of cesium benzene is rather high (some 70% of theory) after 1.5 hours of reaction at -70°. Continued reaction at this temperature results in a gradual increase in 1,4,1′,4′-tetrahydrobiphenyl, while increase of temperature to -35 to 5° results in a rapid increase in this product on hydrolysis. Concurrently the reaction solution changes color from black to a mustard-orange color. Further increase in temperature to 38°, results in appearance of a new set of hydrobiphenyls, like those expected from dicesium biphenyl. We believe that the pertinent reactions are those shown in Scheme VIII. That some 1,4-dihydrobenzene persists in the hydrolysis products, even after warming the reaction mixture to 38°, suggests that this product is formed from another intermediate (likely the yellow-orange anion) besides cesium benzene.

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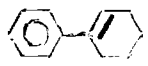
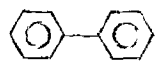
(19) Cf. The reaction of lithium with biphenyl [W. Schlenk and E. Bergmann, Ann. Chem., 463, 92 (1928)].

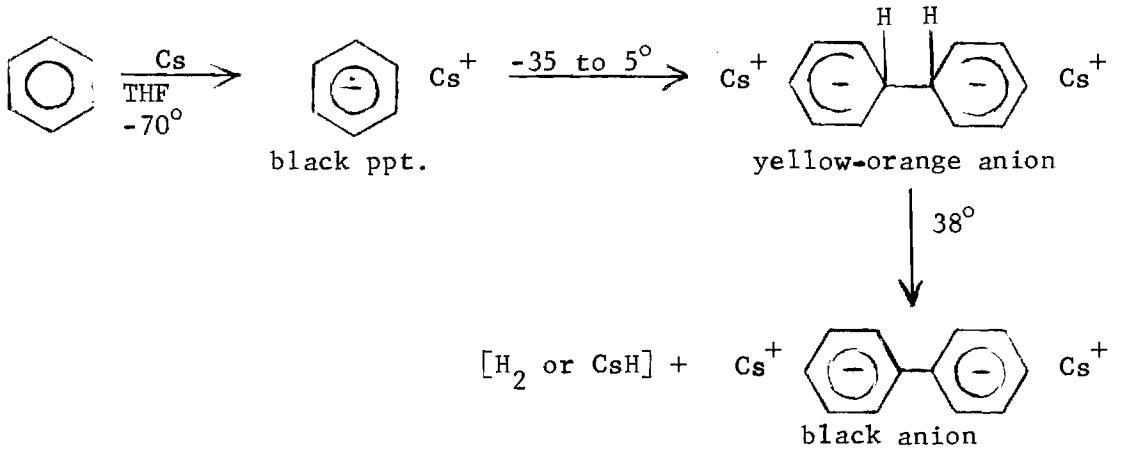
Table II. Reaction of Cesium with Benzene in Tetrahydrofuran

	Procedure[‡] (Color of Mixture)	Products, %[†]						
								Unknown, $C_{12}H_{12}$
(1)	1.5 hr at -70° (Black)	35	0.9	5.6	0	0	0	0
(2)	2.5 hr more at -70° (Black)	30	1.3	12.1	0	0	0	0
(3)	1 hr at -35 ± 5° (Mustard Colored)	23	1.4	30	0	0	0	0
(4)	1 hr at 5 ± 5° (Mustard Colored)	18	-	39	2.3	0.5	1.2	0.1
(5)	1 hr at 38° (Black)	12	2.0	17.5	15.7	6.3	20	3.2

[†]Expressed as 100 times the amount of benzene contained in the given product divided by the maximum amount of benzene which could have reacted on the assumption of a 1:1 molar reaction between benzene and cesium.

[‡]The reaction mixture was subjected to the sequential procedure (1)-(5) and an aliquot quenched with water and analyzed after each procedure.

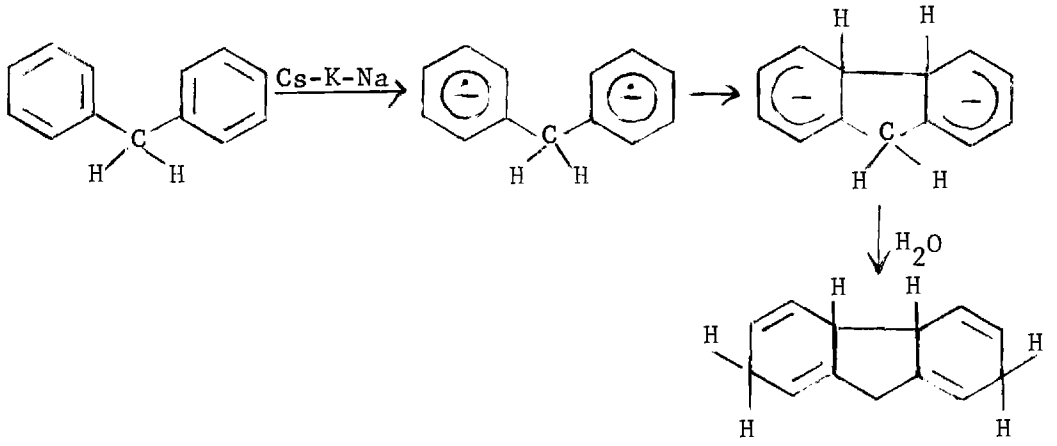
Scheme VIII:



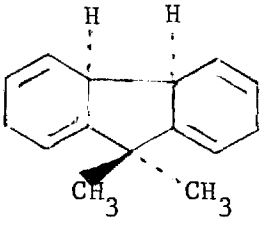
B. Diphenylmethane and 2,2-Diphenylpropane

Diphenylmethane upon reaction with a large excess of Cs-K-Na alloy in THF at -70° for 20 minutes with vigorous stirring, followed by jetting the blue-black solution into an excess of water, gave a volatile product consisting of some 80% of 2,4a,4b,7-tetrahydrofluorene ($C_{13}H_{14}$), 5% of an unknown reduction product, $C_{13}H_{16}$, and some 15% of recovered diphenylmethane. The tetrahydrofluorene can be explained on the basis of Scheme IX.

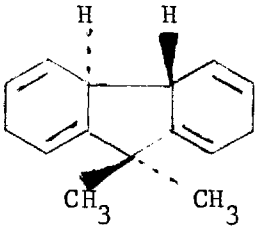
Scheme IX:



The similar eeaction of 2,2-diphenylpropane at -70° for 60 minutes, followed by jetting the deep blue solution into water, gave a volatile product consisting of 95% of 9,9-dimethyl-2,4a,4b,7-tetrahydrofluorene ($C_{15}H_{18}$), 3% of an isomeric $C_{15}H_{18}$ hydrocarbon, and 2% of a further reduction product $C_{15}H_{20}$. The dominant dimethyltetrahydrofluorene, mp 76.5°, according to its nmr spectrum has its methyl groups in slightly different environments and therefore must be the cis isomer A rather than the trans isomer B, which is possibly the minor product. Increasing amounts of the



A



B

minor product (up to 28%) are formed on warming the reaction mixture up to -20° before decomposition with water. The preferred formation of A at low temperatures suggests that a cesium cation is "sandwiched" between the two benzene rings of the anionic precursor and thus maintains the preferred cis stereochemistry in the di-anion.

C. 1,1,1-Triphenylethane[20]

Reaction of 1,1,1-triphenylethane with excess Cs-K-Na alloy at -70° gives a red colored anion (attempts to study the nmr spectrum of this anion

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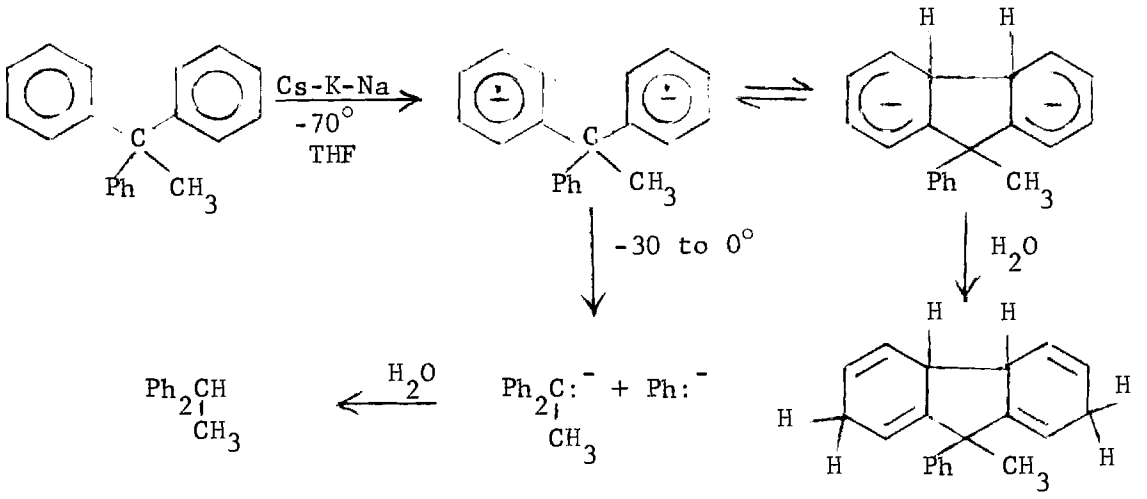
(20) A paper describing much of this work has been submitted for publication.

were unsuccessful because of the slight solubility of the anion at the low temperatures required by its limited thermal stability). The structure of the anion has been deduced on the basis of the structure of its hydrolysis product, 9-methyl-9-phenyl-2,4a,4b,7-tetrafluorene. Further evidence was supplied from the decomposition product with D_2O. On warming to 0°, it was thought that the intermediate red dianion would lose hydride anion to give 9-methyl-9-phenylfluorene (or product derived therefrom); instead, cleavage of a carbon-carbon bond occurred (starting around -30°), such that after 2 hr at 0° some 56% yield of 1,1-diphenylethane was produced upon hydrolysis. The likely pertinent reactions are summarized in Scheme X.

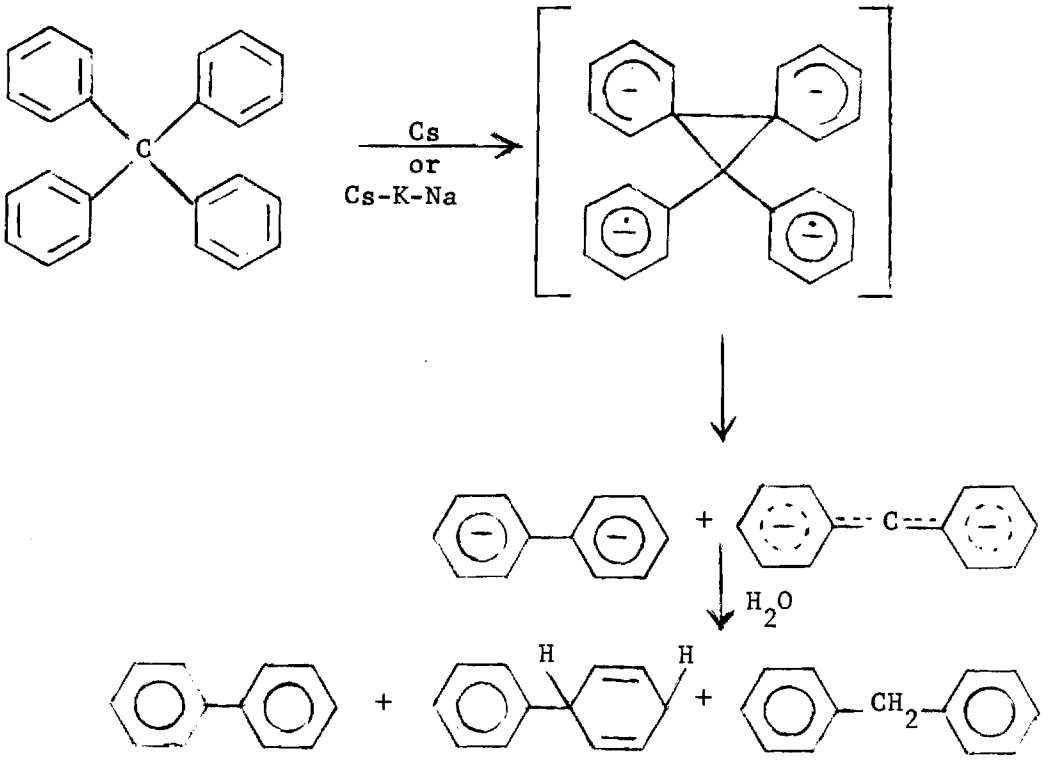
Scheme X:



D. Tetraphenylmethane

Reaction of tetraphenylmethane in THF with excess Cs-K-Na alloy at -67° for 1 hr or with excess cesium metal at 36° gave, after decomposition with water, a mixture of diphenylmethane, biphenyl, dihydrobiphenyl and unidentified products. The chief results may be rationalized according to Scheme XI.

Scheme XI:

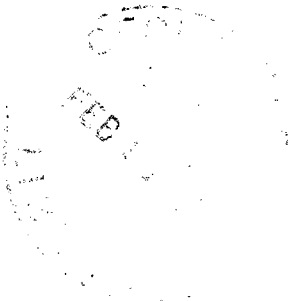


G-33-620

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

CHEMISTRY

TO: Dr. Donald A. Speer
Program Director for Chemical Dynamics
National Science Foundation
Washington, D. C. 20550



FROM: Dr. Erling Grovenstein, Jr.
Principal Investigator
School of Chemistry
Georgia Institute of Technology

SUBJECT: Final Technical Report upon "Chemistry of Carbanions"
NSF Grant No. GP-19251
For Period May 1, 1970-April 30, 1972

Brief Description of Research and Results*

Since comparatively few cases of rearrangement of carbanions are known at present, most of our efforts have been directed toward learning the structural features and reaction conditions necessary for rearrangement. We have discovered the first examples of [1,4] and [1,5] sigmatropic rearrangement of phenyl in the carbanions derived from reactions of 4-chloro-1,1,1-triphenylbutane and 5-chloro-1,1,1-triphenylpentane with alkali metals. A novel di-anion from reaction of cesium alloys with 1,1,1-triphenylalkanes was also discovered in the course of this investigation. A full report of this work should soon appear.[1]

We have now finished a study of the first successful example of a [1,2] anionic sigmatropic rearrangement of an aryl group attached to a primary carbon atom. The example was provided by the reaction of 1-chloro-2-p-biphenylylethane-1,1-d_2 with cesium or potassium metal in tetrahydrofuran at 65°, wherein essentially a 50/50 mixture of 1-p-biphenylylethane-2,2-d_2 and 1-p-biphenylylethane-1,1-d_2 was obtained.[2]

A study of [1,4] anionic sigmatropic rearrangement of the p-biphenylyl group is in progress. Reaction of 4-chloro-1-p-biphenylyl-1,1-diphenyl

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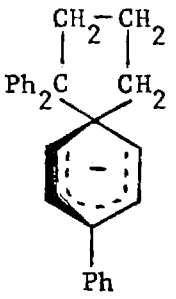
*For further details upon this work see our "Resumé of Progress to Date upon 'Chemistry of Carbanions'" for period of May 1, 1970-September 30, 1971. This resumé was included in our grant renewal application; a copy is enclosed.

butane (1) with potassium or cesium in refluxing tetrahydrofuran gives 4-p-biphenylyl-1,1-diphenylbutyl anion (2) as judged by the products of carbonation and protonation. Since only products of unrearranged structure are obtained when this reaction is run in presence of a little t-butyl alcohol, the 4-p-biphenylyl-4,4-diphenylbutyl anion is formed prior to rearrangement of the p-biphenylyl group. This reaction, therefore, provides the best authenticated example of 1,4-migration of an aryl group in a carbanion (the reaction is also clean-cut and goes in good yield). Even when the reaction of 1 is conducted with Cs-K-Na alloy at -75°, the product after 3 minutes is of rearranged structure (2) with none of the expected 1,1,8-triphenylspiro[4.5]-6,8-decadienyl anion (3) being detected. In contrast, reaction of 4-chloro-1-p-biphenylylbutane with Cs-K-Na alloy at -70°



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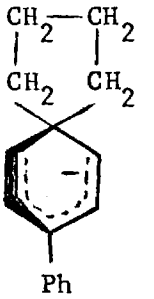

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gives a good yield of 8-phenylspiro[4.5]-6,8-decadienyl anion 4 as deduced from the nmr spectrum and the products of carbonation and protonation. While species similar to 4 have been long suggested as intermediates or transition states in 1,2-migrations of aryl in polyarylalkyllithiums, such carbanions have never previously been isolated from cyclization of ω-arylalkyl anions. We have, therefore, submitted a brief account of this work as a Communication.[3]

We have also discovered a case of [1,2] and/or [3,2] rearrangement of allyl in 2,2-diphenyl-4-pentenyl anion. This system is being studied further with use of carbon-14 to label the end of the allylic system.

Finally cases of apparent [1,2] and [1,4] anionic rearrangement of hydrogen have been uncovered but must be explored further to clarify the mechanistic details.

In a different area, the reactions of cesium and Cs-K-Na alloy with the aromatic hydrocarbons benzene, diphenylmethane, 2,2-diphenylpropane, and tetraphenylmethane have been studied; many of the important results were given in the previous progress report, but much remains to be clarified in this area.

Publications

(1) "Carbanions. XI. Reactions of 4-Chloro-1,1,1-triphenylbutane, 5-Chloro-1,1,1-triphenylpentane, and 1,1,1-Triphenylethane with Alkali Metals; 1,4- and 1,5-Migration of Phenyl," E. Grovenstein, Jr., J. A. Beres, Y.-M. Cheng, and J. A. Pegolotti, J. Org. Chem., 37, to appear ca. June, 1972.

(2) "Carbanions. XII. p-Biphenylyl Migration in Reactions of 1-Chloro-2-p-biphenylylethane-1,1-d_2 with Alkali Metals," E. Grovenstein, Jr., and Y.-M. Cheng, J. Amer. Chem. Soc., 94, to appear ca. September, 1972.

(3) "Carbanions. XIII. 1,4-Migration of the p-Biphenylyl Group; Formation of an Intermediate Spiro Anion," E. Grovenstein, Jr., S. Akabori, and J.-U. Rhee, J. Amer. Chem. Soc., 94, a Communication to the Editor which should appear shortly (1972) [see the enclosed preprint].

Additional publications are planned to cover the other research described in this progress report; in most cases, however, additional experiments need to be performed to complete the work.

Theses

(1) "Syntheses and Rearrangements of Organoalkali Compounds," Ph.D. thesis of Yao-Ming Cheng, Georgia Institute of Technology, September, 1970.

(2) The Ph.D. thesis of Mr. Thomas Longfield (on reactions of cesium and cesium alloys with aromatic hydrocarbons) should be completed by the end of the summer, 1972.

(3) The Ph.D. thesis of Mr. Jung-Ung Rhee (on reactions of alkali metals with 4-chloro-1-p-biphenylyl-1,1-diphenylbutane) should be completed by the end of the summer, 1972.

Inventions or Discoveries

Much of our research effort has been devoted to extending our knowledge of carbanion (and free radical) rearrangements. While this research is of both theoretical and practical importance, it is not in general of the type for which patents are sought. Certain of our work on the "Reactions of Cesium and Cs-K-Na Alloy with Aromatic Hydrocarbons" (see the attached Resumé of Progress to Date for Period May 1, 1970-September 30, 1971, pp A-15 through A-22) may be patentable; however, the Georgia Institute of Technology feels that the best interest of the scientific community will be served by publication of this work rather than by filing a patent application (see the Zerox copy of the letter of Mr. Milton W. Bennett to NSF which is enclosed).

Scientific Collaborators

Mr. Yao-Ming Cheng - completed his Ph.D. thesis under the present grant, 4½ months of support on this grant.

Mr. Jung-Ung Rhee - Ph.D. candidate, 24 months of support on this grant.

Mr. Thomas H. Longfield - Ph.D. candidate, 20 months of support on this grant.

Mr. Auburn B. Cottingham - Ph.D. candidate, 3½ months of support on this grant.

Dr. Craig L. Smith - post-doctoral associate, 2 months of support on this grant.

Comments

This investigation is being continued under NSF Grant No. GP-33367X.

Erling Grovenstein, Jr.
Principal Investigator
May 5, 1972

Enclosures (3)

Resumé of Progress to Date upon "Chemistry of Carbanions"

For Period May 1, 1970-September 30, 1971

NSF Grant No. GP-19251

by Erling Grovenstein, Jr., Principal Investigator

PART I. Studies upon Rearrangements of Carbanions

Since comparatively few cases of rearrangement of carbanions are known at present, most of our efforts have been directed toward learning the structural features and reaction conditions necessary for rearrangement. We report here the first successful example of [1,2] anionic sigmatripic rearrangement[1] of an aryl group attached to a secondary carbon atom, the first examples of [1,4] and [1,5] rearrangement of phenyl and of [1,4] rearrangement of p-biphenylyl, the second example of [1,2] and/or [3,2] sigmatropic rearrangement of an allylic group in an anion containing only carbon and hydrogen, and apparent examples of [1,2] and [1,4] anionic rearrangements of hydrogen. Finally we report in a [1,4] rearrangement of p-biphenylyl the identification by spectroscopic and chemical methods of a fairly stable, novel spiro anion which corresponds in general structure to the type of intermediate long suspected (but never isolable) in [1,2] sigmatropic anionic rearrangements of aryl groups.

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(1) For the definition, theory, and examples of sigmatropic rearrangements, see R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, GmbH, Weinheim, 1971, pp. 114-140.

A. [1,2] Rearrangement of p-Biphenylyl in 2-p-Biphenylylethyl Anion[2]

While [1,2] anionic sigmatropic rearrangements of phenyl and other aryl groups are known,[3] rearrangements in appreciable quantity to date have always involved aryl migration from a quaternary carbon attached to at least one aryl group (or other unsaturated groups[4]) such that the product of migration is normally more stable and is less sterically compressed than the starting organoalkali compound. Cram and Dalton[5] have reported that threo-2-phenyl-3-pentyl methanesulfonate with potassium in 1,2-dimethoxyethane at 25° gave 94.5% of 2-phenylpentane and 5.5% of 3-phenylpentane (product of phenyl migration from a tertiary carbon); threo-3-phenyl-2-pentyl methanesulfonate with sodium in liquid ammonia gave 75% of 3-phenylpentane and 3% of 2-phenylpentane; and 1,1-dideuterio-1-methoxy-2-(1-naphthyl)-ethane and 1,1-dideuterio-2-(1-naphthyl)-ethyl methanesulfonate with potassium in 1,2-dimethoxyethane at 0° gave 1-ethylnaphthalene deuterated only in the methyl group [no detectable rearrangement (less than 5%) accompanied reduction].

In order to test to see if [1,2] sigmatropic anionic rearrangements are restricted to migrations from a quaternary carbon bearing one or more

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(2) This work was reported in part at the XXIII International Congress of Pure and Applied Chemistry, Boston, Mass., July, 1971, p. 112 of Abstracts.

(3) E. Grovenstein, Jr., and co-workers, J. Amer. Chem. Soc., 79, 4985 (1957); ibid., 83, 412 (1961); ibid., 89, 1852 and 2348 (1967). H. E. Zimmerman and co-workers, ibid., 79, 5455 (1957); ibid., 83, 1196 (1961).

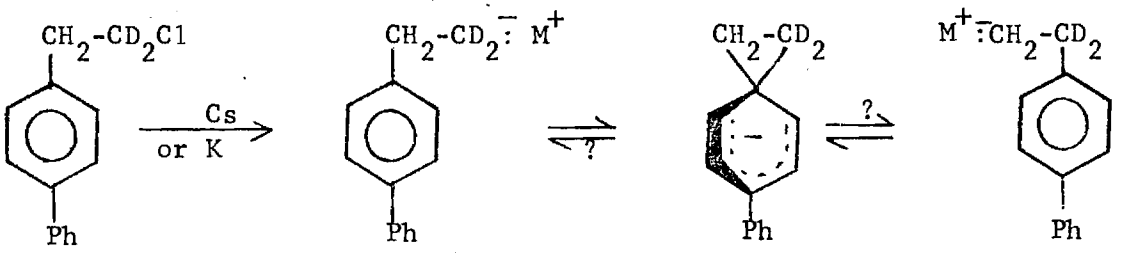
(4) S. W. Staley and J. P. Erdmon, J. Amer. Chem. Soc., 92, 3832 (1970).

(5) D. J. Cram and C. K. Dalton, ibid., 85, 1268 (1963).

unsaturated groups, 1-chloro-2-p-biphenylylethane-1,1-$\underline{d}_2$ has been synthesized and allowed to react with alkali metals under a variety of conditions. With lithium metal in tetrahydrofuran (THF) at -70° this halide gave 2-p-biphenylylethyllithium-1,1-$\underline{d}_2$ containing less than 5% of the rearrangement product 2-p-biphenylylethyllithium-2,2-$\underline{d}_2$ according to nmr analysis of the carboxylic acid obtained on carbonation. When 2-p-biphenylylethyllithium-1,1-$\underline{d}_2$ (prepared at -70°) is held at 1 ± 1° for 9 hours, the final organolithium compound has only some 8% 2-p-biphenylylethyllithium-2,2-$\underline{d}_2$. Attempts to increase the extent of rearrangement by increasing the time resulted (at 2 ± 1° for 16.5 hr) in negligible organolithium compound but dominant 1-p-biphenylylethane-2,2-$\underline{d}_2$ containing only 2% of 1-p-biphenylethane-1,1-$\underline{d}_2$. Attempts to increase the extent of rearrangement at 4° by addition of N,N,N′,N′-tetramethylethylenediamine were also unsuccessful. In conclusion 1-chloro-2-p-biphenylylethane-1,1-$\underline{d}_2$ reacted with lithium at -70° to give essentially pure 2-p-biphenylylethyllithium-1,1-$\underline{d}_2$ which failed to rearrange appreciably (< 10%) under any of the conditions tested.

Reaction of 1-chloro-2-p-biphenylylethane-1,1-$\underline{d}_2$ with Cs-K-Na alloy in THF at -65° gave predominantly p-biphenylylethane which contained 9% and, in a separate run, 22% of product of [1,2] p-biphenylyl rearrangement. Reaction with cesium in THF at 65° gave a product which consisted essentially of a 50/50 mixture of p-biphenylylethane-2,2$\underline{d}_2$ and -1,1-$\underline{d}_2$; a similar result was obtained with potassium in THF at 65°. Thus it is concluded that in reaction with cesium and potassium in refluxing THF, the two methylene groups become equibrated, likely by way of a symmetrical intermediate such as II (see Scheme I):

Scheme I:



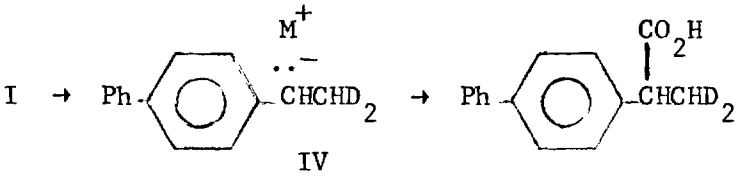
I II III

A number of questions immediately arise concerning the validity of Scheme II. Does cyclization occur in an anion or a free radical? Is cyclization concerted such that intermediate I is not really formed? To help answer these questions the reaction of 1-chloro-2-p-biphenylyl-1,1-d_2 with potassium was carried out in refluxing THF having a little t-butyl alcohol and, in a second very similar experiment t-BuOD. Mass spectroscopic and nmr analyses of the p-biphenylylethane produced, showed that less than 19% rearrangement of p-biphenylyl occurred in presence of t-butyl alcohol. t-Butyl alcohol should be less effective in trapping alkyl free radicals than tetrahydrofuran[6] but much more effective in protonation of carbanions, consequently we conclude that, since addition of t-butyl alcohol nearly stops the rearrangement, essentially all of the 2-p-biphenylethyl must exist as an anion (doubtlessly as I) prior to cyclization. We believe, therefore, that it is the anion I which undergoes cyclization to II.

The present results do not require that the cyclic anion II undergoes ring opening to give I and III, however attractive this may seem. Indeed in one experiment with cesium in THF at reflux, a by-product 2-p-biphenylylpropanoic acid-3,3-d_2 was obtained (in 6% yield) whose isotopic labeling indicates that it could not have come from II, an equilibrium mixture of

(6) Cf. W. A. Pryor, Chem. & Eng. News, June 7, pp 42-43 (1971).

I and III, or from the 50/50 mixture of isotopically labeled p-biphenylylethanes which were isolated from the run. The most likely interpretation is that the 2-p-biphenylylpropanoic acid-3,3-d_2 came from carbanion I by way of IV



If this interpretation is correct, then the p-biphenylylethane which was isolated evidently came from protonation of the cyclic intermediate II. This conclusion needs to be verified.

In conclusion the ready migration of p-biphenylyl in 2-p-biphenylylethylpotassium and -cesium constitutes the first example[7] of a [1,2] anionic sigmatropic rearrangement of an aryl group attached to a secondary carbon atom. Cram and Dalton's lack of success[5] in the 1-naphthyl system may be due to the more acidic character of the solvent (1,2-dimethoxyethane) which they used.

B. [1,4] and [1,5] Rearrangement of Phenyl in 4,4,4-Triphenylbutyl and 5,5,5-Triphenylamyl Anions

With potassium metal in THF at reflux temperature, 4-chloro-1,1,1-triphenylbutane gives chiefly 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene; with Cs-K alloy at -49°, the initial product is 1,1,1-triphenylbutane along with some 9% of 1,1,4-triphenylbutyl anion, the product of [1,4] phenyl migration. Reaction of 5-chloro-1,1,1-triphenylpentane with potassium or with

(7) A full paper on this work is in process of preparation.

Cs-K and Cs-K-Na alloys in THF gives primarily 1,1,1-triphenylpentane as initial product along with (for cesium alloys) some 6% of a product of [1,5] migration of phenyl. These major findings were reported under our previous grant (NSF GP-8309). The chief new work in this area was to confirm and clarify[8] some of the unusual results (such as the differences between potassium and the cesium alloys on the 4-chloro compound). A full paper describing this work has now been submitted for publication.

C. [1,4] Rearrangement of p-Biphenylyl in 4-Biphenylyl-4,4-diphenylbutyl Anion[2]

While [1,4] rearrangement of phenyl was obtained in the 4,4,4-triphenylbutyl system (see previous section), the amount of this rearrangement did not exceed 9% under the most favorable conditions studied. In order to learn more concerning the mechanism of such [1,4] rearrangements, a new system derived from 4-chloro-1-(p-biphenylyl)-1,1-diphenylbutane has been studied since, in view of the demonstrated[9] greater migratory aptitude of p-biphenylyl over m-biphenylyl and likely over phenyl, this system was expected to give more facile [1,4] rearrangement of p-biphenylyl than the previous system did of phenyl. This expectation has now been fully confirmed.

Reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane with lithium in THF at -70° gave upon hydrolysis a 76 to 24 ratio of 1-p-biphenylyl-1,1-diphenylbutane to 4-p-biphenylyl-1,1-diphenylbutane; upon standing for 4 hr at

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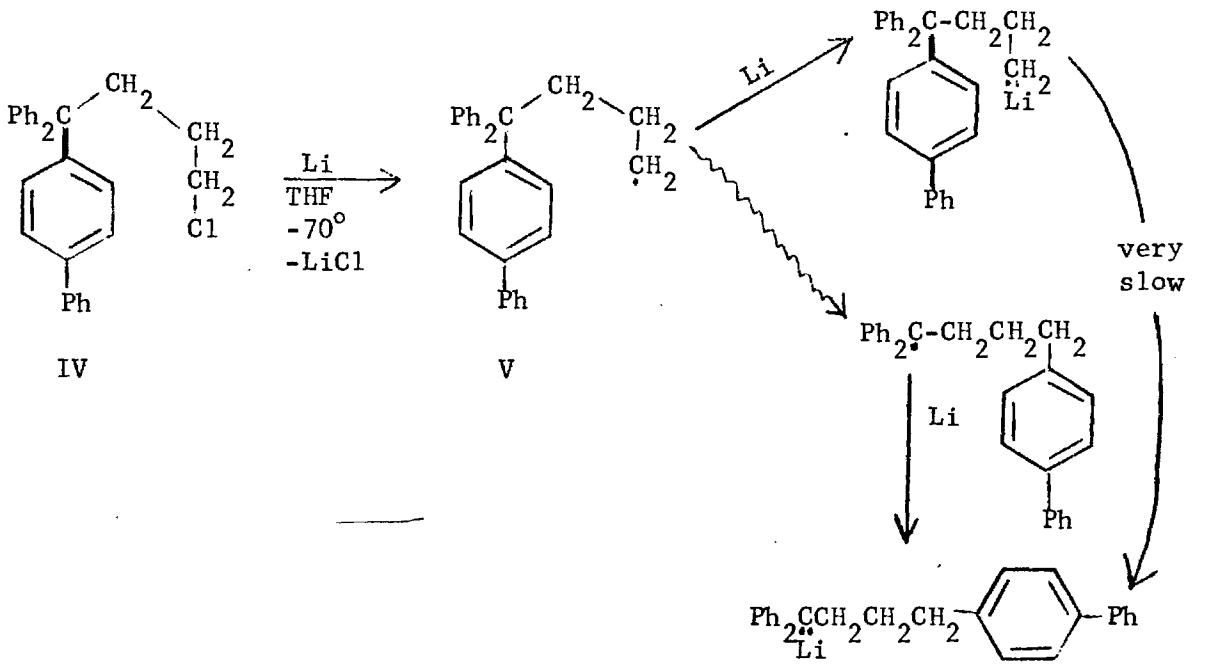
(8) Work of Mr. William B. Shannon, N.S.F. Undergraduate Science Summer Trainee, 1971.

(9) E. Grovenstein, Jr., and G. Wentworth, J. Amer. Chem. Soc., 89, 2348 (1967).

0°, the solution gave a 66 to 34 ratio of non-rearranged to rearranged products. Since 24% rearrangement took place during the reaction with lithium at -70° but only 10% more rearrangement at 0°, it is concluded that 4-p-biphenylyl-4,4-diphenylbutyllithium rearranges very slowly even at 0°; therefore the larger quantity of rearrangement at -70° must be via another process — we suggest that this is rearrangement[10] of an intermediate radical V (see Scheme II):

Scheme II:



Reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane with potassium or cesium in THF at 65° or with Cs-K-Na alloy in THF at -75° gives in each case, upon carbonation, a high yield of 5-p-biphenylyl-2,2-pentanoic acid. These results suggest that both 4-p-biphenylyl-4,4-diphenylbutylcesium and

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(10) See E. Grovenstein, Jr., and Y.-M. Cheng [Chem. Comm., 101 (1970)] for an analogous rearrangement during reaction of neophyl chloride with lithium.

-potassium undergo very ready [1,4] rearrangement of p-biphenylyl even at -75° (4 min reaction time); alternatively rearrangement could take place in the corresponding free redical V as observed with lithium metal. To distinguish between these possibilities the experiments summarized in Table I were performed. While the results are somewhat complicated by reduction of the biphenyl nucleus, this table shows that, whereas the chloride reacts with potassium in THF with essentially complete [1,4] rearrangement of the biphenylyl group, in presence of excess t-butyl alcohol rearrangement is completely blocked. With the less effective proton donor, triethylcarbinol, rearrangement is much more extensive; with the still less acidic n-butylamine, rearrangement is almost as complete as in pure tetrahydrofuran. Since the extent of rearrangement varies inversely with the proton donor ability of the reaction medium (not the hydrogen atom donor ability which was approximately constant in Exp. 1-5 of Table I), the results agree well with the idea that it is a carbanion (or organoalkali compound) which is undergoing rearrangement and which is trapped prior to rearrangement by addition of weak acids (see Scheme III).

Scheme III:

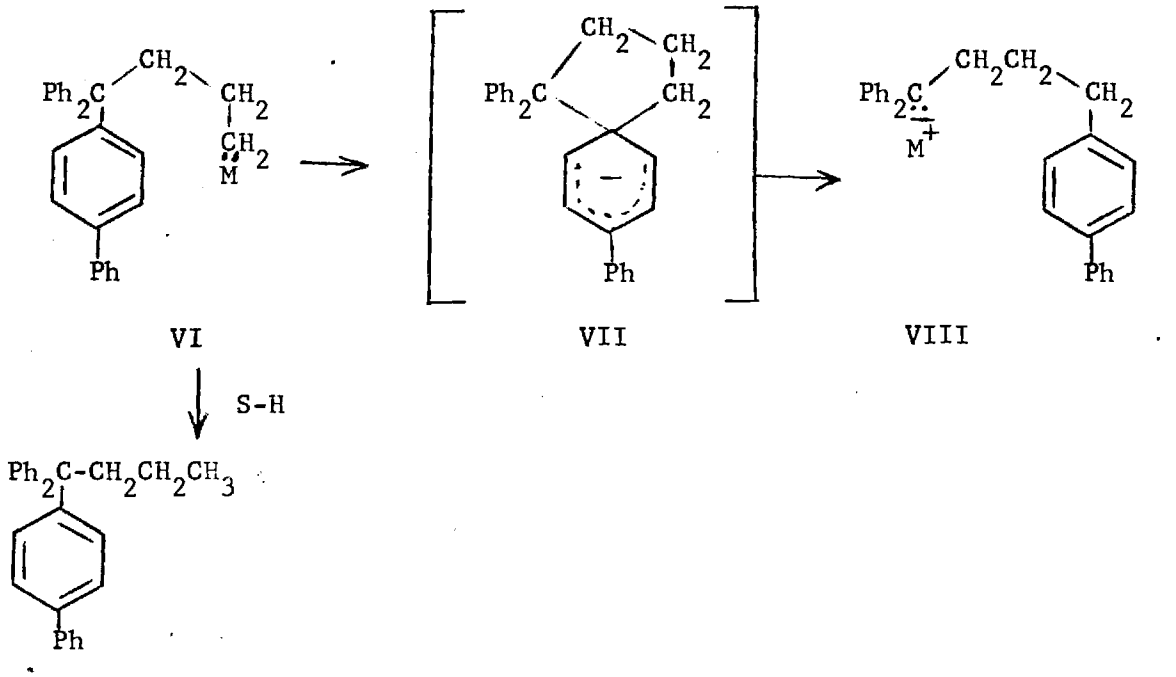
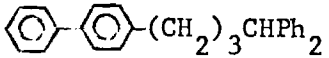
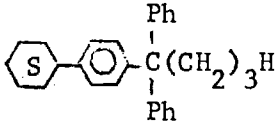
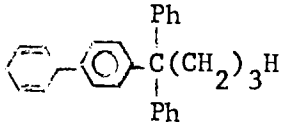
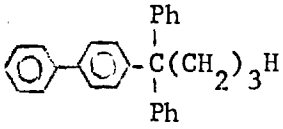


Table I. Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Alkali Metals in Various Media

Exp. No.	Conditions	Products, %			
					
(1)	React with K in THF at 65° and then add CH_3OH	97.6	0	0	1.4[a]
(2)	2.6 mmoles RCl with 5.8 mg-at. of K + 13 mmoles t-BuOH in THF at 65°	0	13.8	-	12.5[b]
(3)	The reaction mixture from (2) treated 7 times successively with 6 mg-at. of K and 6 mmoles t-BuOH at 65° in THF	0	90	5.8	3.4
(4)	2.3 mmoles RCl with 7.1 mg-at. of K and 6.8 mmoles of $(CH_3CH_2)_3COH$ at 65° in THF	52	0	8	7[c]
(5)	2.7 mmoles RCl with 5.8 mg-at. of K and 12.5 mmoles of n-$BuNH_2$ at 65° in THF and then addition of CH_3OH	95	0	0	4.5
(6)	React with Na in dioxane at 101°	8	0	0	92
(7)	React with K in dioxane at 101° and then addition of EtOH	75	0	0	0[d]

[a]There was also found 0.8% of $Ph_2CHCH_2CH_2CH_3$ and 0.2% of p-$PhC_6H_4CHPh_2$. [b]The remainder was unreacted RCl. [c]The remainder consisted of 25% of unreacted RCl and 9% of an unknown. [d]The remainder consisted of 12% of an unknown hydrocarbon and the rest non-volatile (glpc) material; carbonation of a portion gave 26% yield of a complex mixture of acids and 74% yield of the same volatile neutral products.

In Exp. 6 and 7 of Table I, the effect of change of solvent from tetrahydrofuran to dioxane and change of alkali metal from potassium to sodium is investigated. In both tetrahydrofuran and dioxane, potassium reacts with 4-chloro-1-p-biphenylyl-1,1-diphenylbutane to give almost exclusively products of [1,4] rearrangement of p-biphenylyl; in tetrahydrofuran at 65° the product is the corresponding 4-p-biphenylyl-1,1-diphenylbutyl anion whereas in dioxane it is predominantly the corresponding hydrocarbon. Evidently dioxane at 101° is more acidic (toward carbanions) than THF at 65° (although THF is a better hydrogen atom donor than dioxane[6]). In contrast to potassium, sodium metal in dioxane gives predominantly the non-rearranged hydrocarbon. Taken along with the earlier experiments with lithium and cesium, the present results show that the ease of [1,4] anionic rearrangement of p-biphenylyl increases along the series: RLi < RNa < RK ≃ RCs.

D. Cyclization of 4-p-Biphenylylbutyl Anion; Isolation of the Intermediate in [1,4] Rearrangement of p-Biphenylyl[11]

Both in the [1,2] and [1,4] rearrangements of phenyl and p-biphenylyl spirocyclic anionic intermediates have been postulated (see II in Scheme I and VII in Scheme III); however, no direct evidence for these transient intermediates has ever been obtained such that it is unclear whether structures such as II and VII correspond to transition states or reaction intermediates. Evidence in favor of the latter interpretation has now been obtained.

Reaction of 1-chloro-4-p-biphenylylbutane-1,1-d_2 with lithium metal in THF at -70° followed by carbonation gave a mixture of acids consisting

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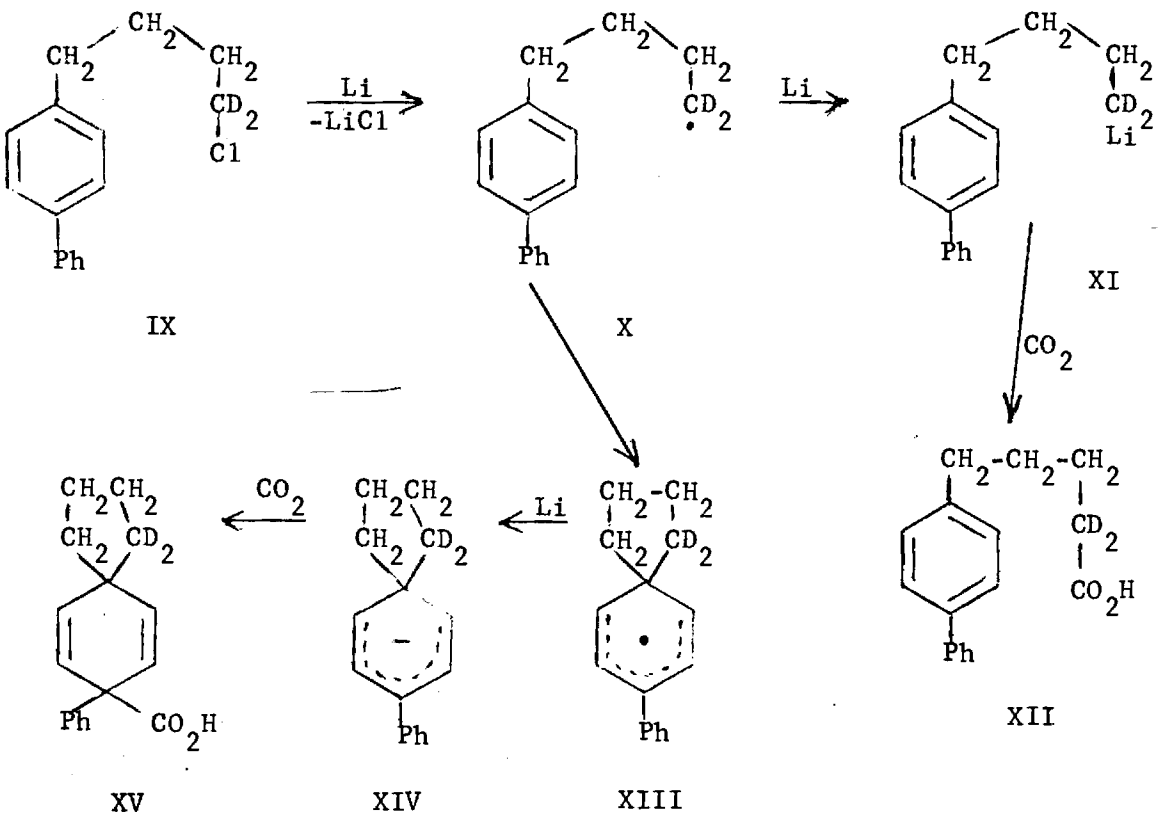
(11) This work (by Dr. S. Akabori) was partially supported by the present NSF grant but was primarily supported by funds supplied by the School of Chemistry, Georgia Institute of Technology.

of 65% of XII and 35% of XV (see Scheme IV). Since the straight chain acid XII was uniquely labeled with deuterium as shown, it is obvious that no symmetrical spiro intermediate such as XIV or XIII could have been its precursor. Since the yield of spiro products was not increased on warming the present mixture of organolithium compounds XI and XIV to 5°, it seems unlikely that XI can yield XIV at -70°. Hence it appears that the rearranged product XIV was formed via rearrangement of the radical X rather than by rearrangement of an organoalkali compound.

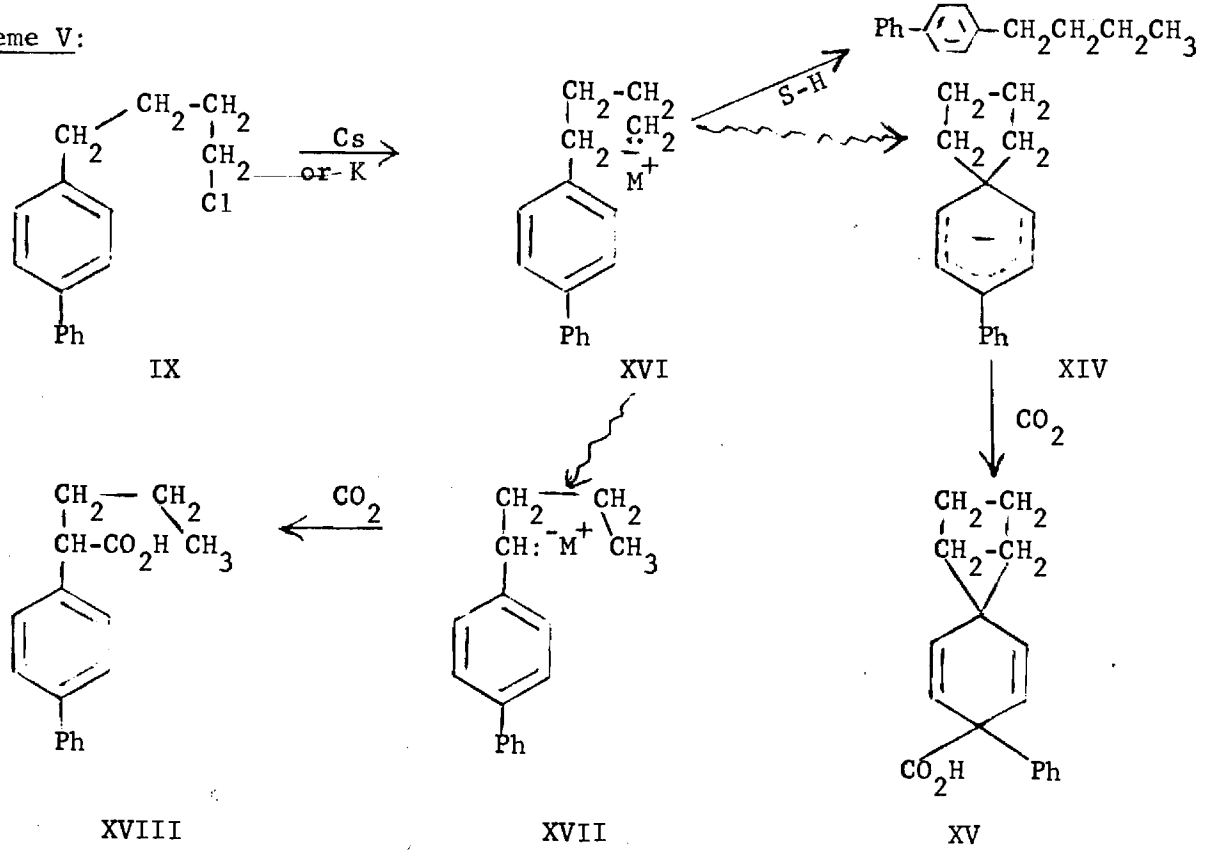
Scheme IV:



In contrast to lithium reaction of cesium and potassium with 1-chloro-4-p-biphenylylbutane in THF at 65° gave upon carbonation 80/20 and 76/24

ratios of acids XV/XVIII where XVIII appears to be 2-p-biphenylylpentanoic acid. Repetition of this reaction with excess Cs-K-Na alloy at -70° gave a 96% yield of acids in which the ratio of XV to XVIII was 97/3. Thus a nearly quantitative yield of spiro anion XIV has been obtained. The structure of this red anion which is reasonably stable in THF at room temperature has been confirmed by study of its nmr spectrum in perdeuterio-tetrahydrofuran. Since 1-chloro-4-p-biphenylylbutane-1,1-d_2 reacts with sodium in dioxane at 101° to give only 1-p-biphenylylbutane-4,4-d_2, evidently reaction with sodium gives first the 4-p-biphenylylbutyl anion XVI which is subsequently protonated by solvent to give 1-p-biphenylylbutane prior to cyclization. Presumably reactions with Cs and K involve the same intermediate anion XVI which rearranges in large part to the spiro anion XIV and in part to the benzylic anion XVII (see Scheme V).

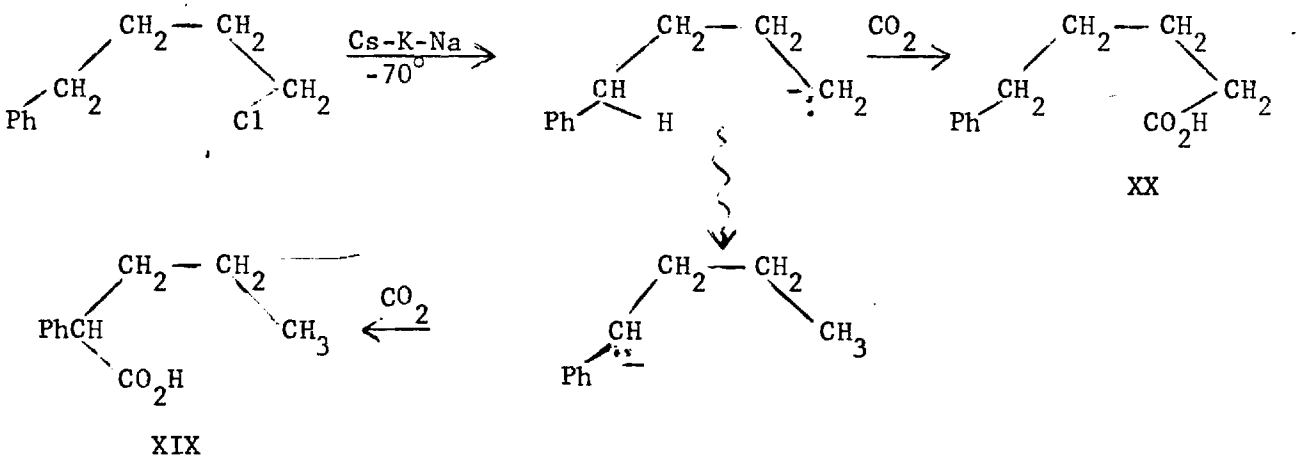
Scheme V:



E. [1,4] Rearrangement of Hydrogen in 4-Phenylbutyl Anion[11]

Addition of 1-chloro-4-phenylbutane to excess Cs-K-Na alloy at -70° in THF over a period of three minutes followed by stirring for one minute before carbonation gave 74% yield of acidic compounds. Analysis of these by glpc as methyl esters indicated that the acids contained 86% yield of 2-phenyl-1-pentanoic acid (XIX), 2.5% of 4-phenyl-1-pentanoic acid (XX), and small quantities of three unknowns. Thus in sharp contrast to the 4-p-biphenylyl-butyl anion which primarily undergoes cyclization to XIV, the 4-phenylbutyl anion undergoes what appears to be a [1,4] rearrangement of hydrogen (see Scheme VI).

Scheme VI:



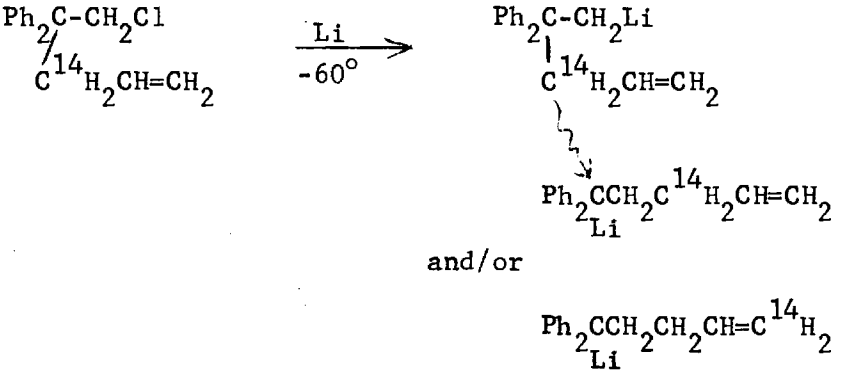
Under comparable conditions at -70° with 4-p-biphenylylbutyl anion only some 3% of [1,4] rearrangement of hydrogen occurred (see earlier discussion). We would emphasize the extreme rapidity of the present [1,4] rearrangement. We assume that the present rearrangement is intramolecular, but this remains to be established. As far as we are aware, a rearrangement of the present type across a saturated system has never been previously reported for carbanions.

In the realm of free radical reactions, [1,5] and, less commonly, [1,6] migrations of hydrogen from carbon to nitrogen have been reported in the Hofmann-Löffler reaction of N-haloamines in sulfuric acid solution. For an apparent example of [1,2] migration of a proton in 2-p-biphenylylethyl-1,1-d_2 anion see Section I A of this report.

F. [1,2] and/or [3,2] Rearrangement of Allyl in 2,2-Diphenyl-4-pentenyl Anion[12]

2,2-Diphenyl-4-pentenyllithium was prepared by reaction of the corresponding chloride with lithium in THF at -60°. Upon warming to 0° the lithium compound underwent rearrangement go give 1,1-diphenyl-4-pentenyllithium as deduced from the products of carbonation and protonation. Thus the allyl group has a greater migratory aptitude than a phenyl group in the present system. The present work is in process of repetition with one end of the allylic system labeled with carbon-14 in order to discover if this is a [1,2] and/or a [3,2] rearrangement of allyl (see Scheme VII).

Scheme VII:



(12) This work (by Mr. A. B. Cottinghem) was only partially supported by funds from the present NSF grant.

The present work provides the second example of migration of allyl in an anion containing only carbon and hydrogen and seems to offer advantages over the previous system,[13] especially in the use of carbon-14 rather than two methyl groups to label the ends of the allyl system.

PART II. Reactions of Cesium and Cs-K-Na Alloy with Aromatic Hydrocarbons

In view of the reluctance of benzene to add Na-K Alloy[14] to give an appreciable quantity of radical anion, it is surprising to read that cesium reacts with excess benzene to give a black precipitate. Hackspill[15] who first observed this reaction suggested that this precipitate was phenylcesium formed by the process:

$$3\ C_6H_6 + 2\ Cs \rightarrow 2\ C_6H_5Cs + C_6H_8$$

Later Hackspill[16] questioned the structure of this product and noted that the compound merited further attention. Subsequently de Postis,[17] working in Hackspill's laboratory, came to the conclusion that the black compound had the empirical formula of $C_6H_6Cs_6$ and was a loose addition compound of benzene with cesium, since it was attacked by water with evolution of hydrogen, did not react with gaseous CO_2, and failed to give "normal" alkylation products with alkyl halides. Other benzenoid compounds such as t-butylbenzene and,

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(13) For the first example, which was reported after our work was well underway, see J. E. Baldwin and F. J. Urban, Chem. Comm., 165 (1970).

(14) R. G. Kooser, W. V. Volland, and J. H. Freed, J. Chem. Phys., 50, 5243 (1969).

(15) L. Hackspill, Eighth International Congress of Applied Chemistry (New York), 2, 113 (1912); Ann. chim. et phys., [8], 28, 653 (1913).

(16) L. Hackspill, Helv. Chim. Acta, 11, 1026 (1928).

(17) J. de Postis, Eleventh International Congress of Pure and Applied Chemistry (London), 5, 867 (1947). See also L. Hackspill, "Nouveau Traité de Chimie Minerale," P. Pascal, 3, 125 (1956).

under certain conditions, cumene and diphenylmethane were reported[17] to form similar addition compounds with cesium. Since a cesium cation is about the same size as a benzene ring, it was suggested that steric factors prevented six cesium atoms from interacting strongly with a single benzene nucleus.

In the course of our work upon carbanion rearrangements, we have undertaken to prepare carbanions by interaction of cesium metal and Cs-K-Na alloy with arylalkyl chlorides. This work led to some unexpected results.[18] In light of this and the peculiar reports of Hackspill and de Postis, we have undertaken a rather extensive study of the interaction of cesium and Cs-K-Na alloy with aromatic hydrocarbons.

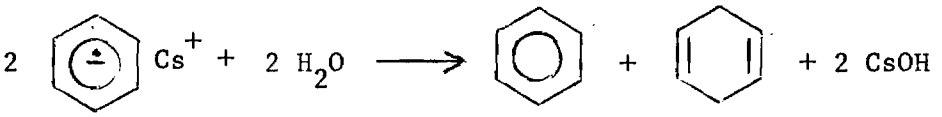
A. Benzene

In a preliminary investigation, we find that cesium reacts at 40° with excess benzene (the latter as reaction medium) to give a black precipitate which, after washing with isooctane, has about a one to one ratio of bound cesium to benzene (if unreacted cesium metal, as measured by hydrogen evolution on hydrolysis, is subtracted from the total cesium). Since the black product gives essentially no esr signal, it cannot be a radical anion. Reaction of the black precipitate with iodine gave a mixture in which 27% of the benzene rings were present as benzene and 73% were present as biphenyl. Hydrolysis of the black precipitate gave a product which contained 14% of the benzene rings as benzene, 15.5% as 1,4-dihydrobenzene, and the remainder as biphenyl, dihydrobiphenyl, tetrahydrobiphenyls, and a little phenylcyclo-

(18) Unpublished work with J. A. Beres, Y.-M. Cheng, and J. A. Pegolotti.

hexane. These products suggest that the black precipitate is in good part the di-cesium addition product of biphenyl.[19]

In a still more informative experiment, finely divided cesium was allowed to react with excess benzene in THF at -70°. The results are summarized in Table II. On the likely assumption that 1,4-dihydrobenzene is formed from a one-to-one adduct (cesium benzene) according to the overall stoichiometric equation,



it is seen that initially the yield of cesium benzene is rather high (some 70% of theory) after 1.5 hours of reaction at -70°. Continued reaction at this temperature results in a gradual increase in 1,4,1′,4′-tetrahydrobiphenyl, while increase of temperature to -35 to 5° results in a rapid increase in this product on hydrolysis. Concurrently the reaction solution changes color from black to a mustard-orange color. Further increase in temperature to 38°, results in appearance of a new set of hydrobiphenyls, like those expected from dicesium biphenyl. We believe that the pertinent reactions are those shown in Scheme VIII. That some 1,4-dihydrobenzene persists in the hydrolysis products, even after warming the reaction mixture to 38°, suggests that this product is formed from another intermediate (likely the yellow-orange anion) besides cesium benzene.

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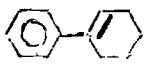
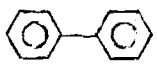
(19) Cf. The reaction of lithium with biphenyl [W. Schlenk and E. Bergmann, Ann. Chem., 463, 92 (1928)].

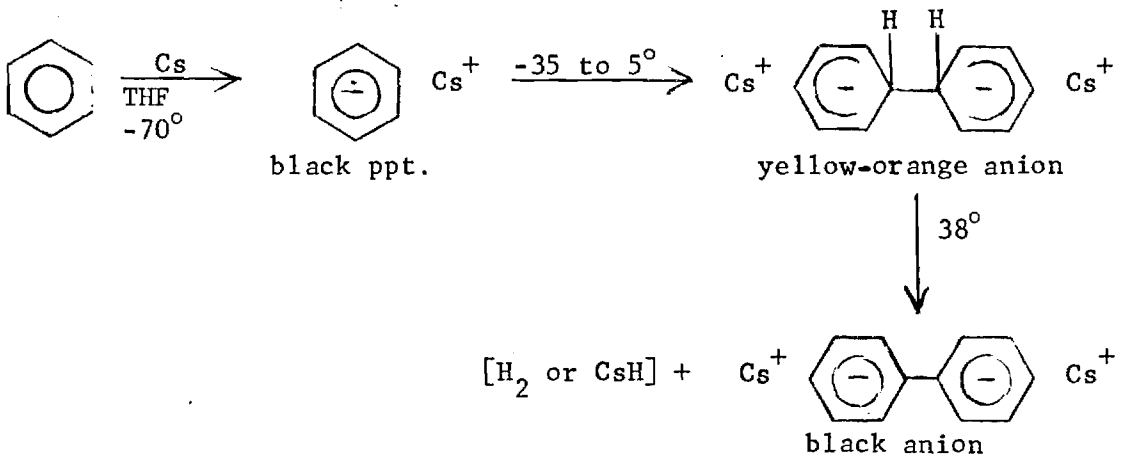
Table II. Reaction of Cesium with Benzene in Tetrahydrofuran

	Procedure[‡] (Color of Mixture)	Products, %[†]						
								Unknown, $C_{12}H_{12}$
(1)	1.5 hr at -70° (Black)	35	0.9	5.6	0	0	0	0
(2)	2.5 hr more at -70° (Black)	30	1.3	12.1	0	0	0	0
(3)	1 hr at -35 ± 5° (Mustard Colored)	23	1.4	30	0	0	0	0
(4)	1 hr at 5 ± 5° (Mustard Colored)	18	-	39	2.3	0.5	1.2	0.1
(5)	1 hr at 38° (Black)	12	2.0	17.5	15.7	6.3	20	3.2

[†]Expressed as 100 times the amount of benzene contained in the given product divided by the maximum amount of benzene which could have reacted on the assumption of a 1:1 molar reaction between benzene and cesium.

[‡]The reaction mixture was subjected to the sequential procedure (1)-(5) and an aliquot quenched with water and analyzed after each procedure.

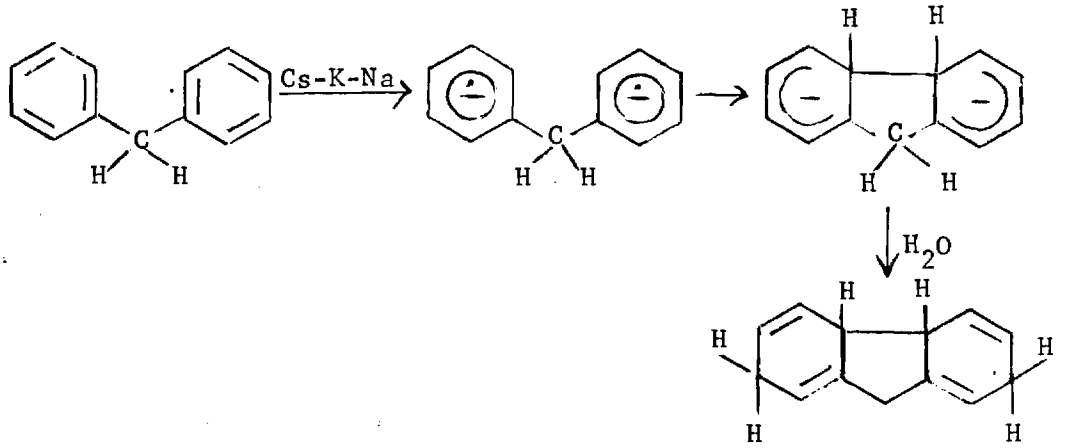
Scheme VIII:



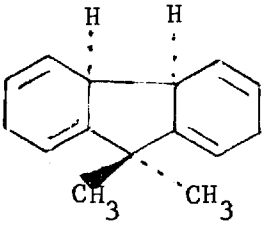
B. Diphenylmethane and 2,2-Diphenylpropane.

Diphenylmethane upon reaction with a large excess of Cs-K-Na alloy in THF at -70° for 20 minutes with vigorous stirring, followed by jetting the blue-black solution into an excess of water, gave a volatile product consisting of some 80% of 2,4a,4b,7-tetrahydrofluorene ($C_{13}H_{14}$), 5% of an unknown reduction product, $C_{13}H_{16}$, and some 15% of recovered diphenylmethane. The tetrahydrofluorene can be explained on the basis of Scheme IX.

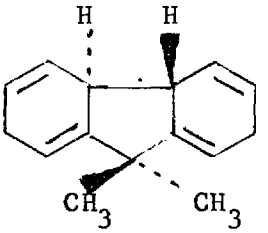
Scheme IX:



The similar eeaction of 2,2-diphenylpropane at -70° for 60 minutes, followed by jetting the deep blue solution into water, gave a volatile product consisting of 95% of 9,9-dimethyl-2,4a,4b,7-tetrahydrofluorene ($C_{15}H_{18}$), 3% of an isomeric $C_{15}H_{18}$ hydrocarbon, and 2% of a further reduction product $C_{15}H_{20}$. The dominant dimethyltetrahydrofluorene, mp 76.5°, according to its nmr spectrum has its methyl groups in slightly different environments and therefore must be the cis isomer A rather than the trans isomer B, which is possibly the minor product. Increasing amounts of the



A



B

minor product (up to 28%) are formed on warming the reaction mixture up to -20° before decomposition with water. The preferred formation of A at low temperatures suggests that a cesium cation is "sandwiched" between the two benzene rings of the anionic precursor and thus maintains the preferred cis stereochemistry in the di-anion.

C. 1,1,1-Triphenylethane[20]

Reaction of 1,1,1-triphenylethane with excess Cs-K-Na alloy at -70° gives a red colored anion (attempts to study the nmr spectrum of this anion

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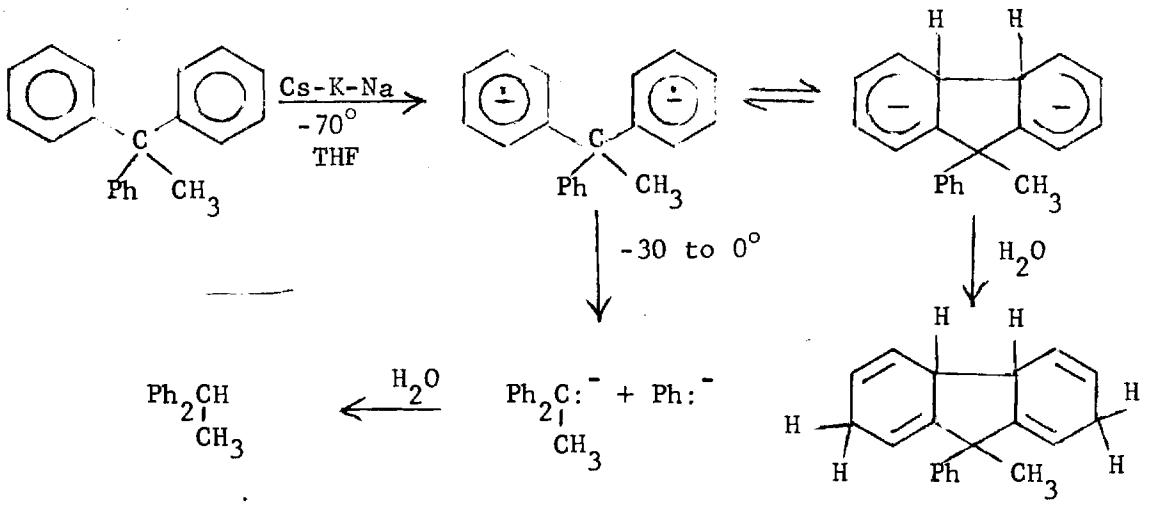
(20) A paper describing much of this work has been submitted for publication.

were unsuccessful because of the slight solubility of the anion at the low temperatures required by its limited thermal stability). The structure of the anion has been deduced on the basis of the structure of its hydrolysis product, 9-methyl-9-phenyl-2,4a,4b,7-tetrafluorene. Further evidence was supplied from the decomposition product with D_2O. On warming to 0°, it was thought that the intermediate red dianion would lose hydride anion to give 9-methyl-9-phenylfluorene (or product derived therefrom); instead, cleavage of a carbon-carbon bond occurred (starting around -30°), such that after 2 hr at 0° some 56% yield of 1,1-diphenylethane was produced upon hydrolysis. The likely pertinent reactions are summarized in Scheme X.

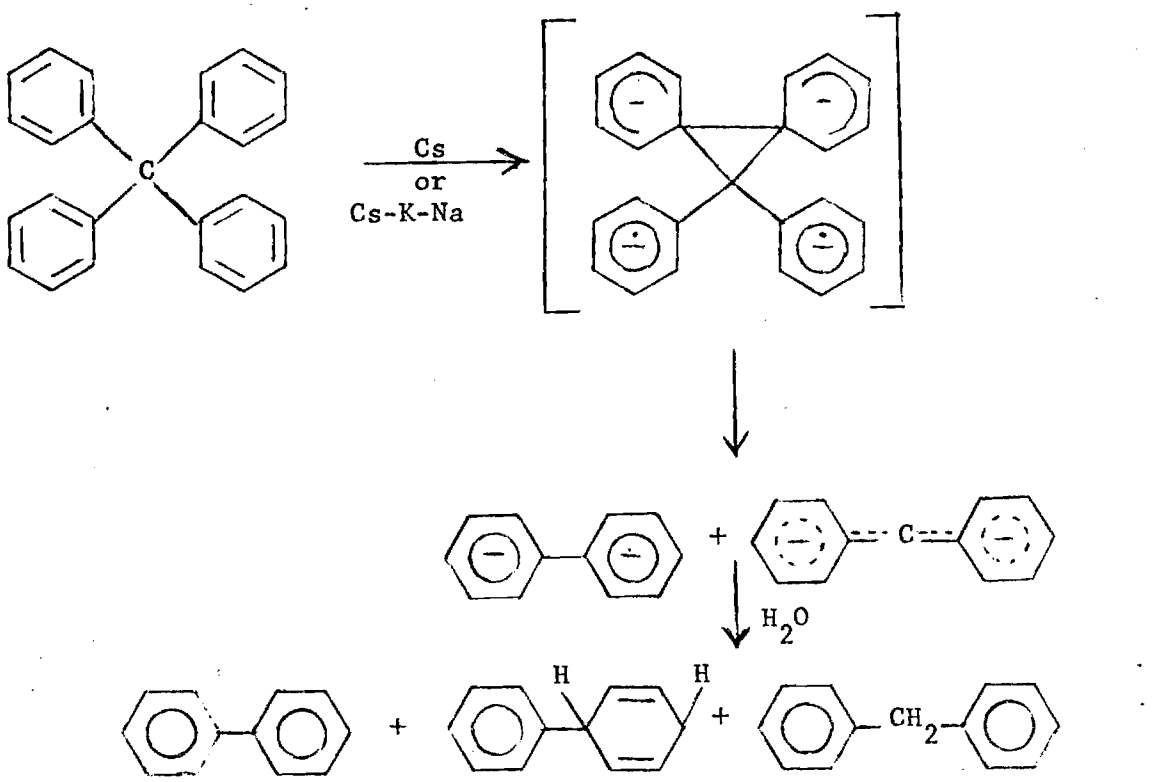
Scheme X:



D. Tetraphenylmethane

Reaction of tetraphenylmethane in THF with excess Cs-K-Na alloy at -67° for 1 hr or with excess cesium metal at 36° gave, after decomposition with water, a mixture of diphenylmethane, biphenyl, dihydrobiphenyl and unidentified products. The chief results may be rationalized according to Scheme XI.

Scheme XI:



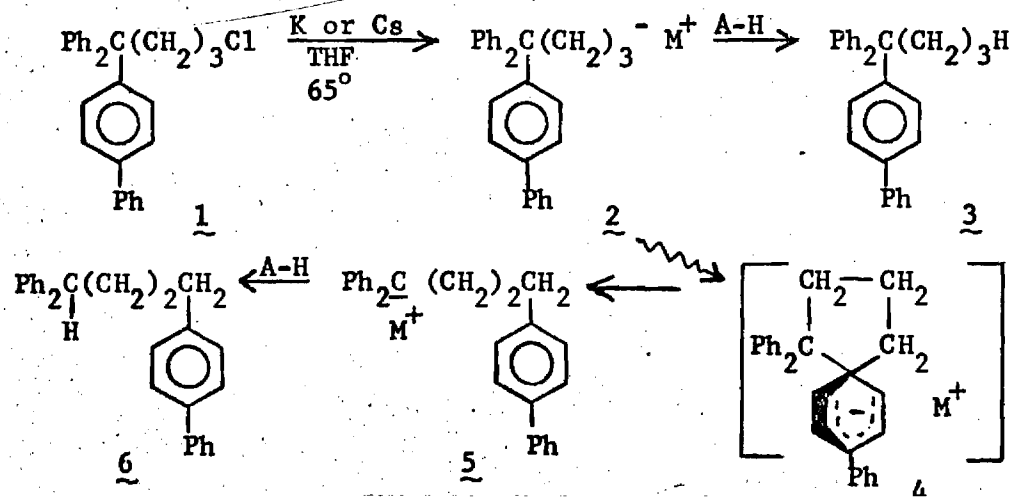
[To appear in J. Amer. Chem. Soc.]

Carbanions. XIII. 1,4-Migration of the p-Biphenylyl Group; Formation of an Intermediate Spiro Anion

Sir:

Whereas 1,4-migration of the phenyl group occurs only as a minor process in the reaction of 4-chloro-1,1,1-triphenylbutane with alkali metals,[1] 1,4-migration of the p-biphenylyl group is now found to be the major process in similar reactions of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1). The chloride[2] (1), mp 99-100°, was prepared by reaction of p-biphenylyldiphenylmethylsodium[3] with excess of 1-bromo-3-chloropropane. Addition of 1 over a 10 min period to finely divided potassium (in a Morton high-speed stirring apparatus) in boiling tetrahydrofuran (THF) gave a dark red solution which upon carbonation yielded 5-p-biphenylyl-2,2-diphenylpentanoic acid, mp 191-192°, or upon decomposition with methanol gave 4-p-biphenylyl-1,1-diphenylbutane (6), mp 81-82°, containing only some 1% of 1-p-biphenylyl-1,1-diphenylbutane (3), mp 94.5-95°.[4] Reaction of 1 with finely divided cesium over a 4 min period in boiling THF gave the same rearranged carbanion according to analysis of the products from carbonation and protonation. These results may be explained according to Scheme I.

Scheme I



In view of the fact that phenyl groups are known to undergo 1,4-migrations in free radicals,[5] to establish Scheme I it is necessary to show that formation of carbanion 2 precedes rearrangement of the p-biphenylyl group. In experiments designed to trap the intermediate anion 2, the chloride 1 was allowed to react at 65° in THF with increments of potassium and t-butyl alcohol, the latter always in slight excess. Analysis of the reaction mixture at intervals revealed that 1-p-biphenylyl-1,1-diphenylbutane 3 was an initial product of reaction; the maximum yield of 3 was some 18%, but this product largely disappeared with continued reduction by excess potassium. The final product consisted of 3% of 3, 90% of 1-(p-cyclohexylphenyl)-1,1-diphenylbutane[2] (7) (mp 100.5-102°), and 6% of an unknown 8. Compound 8 is evidently a 1,4-dihydro derivative of 3 since (unlike 7 which was unaffected) it gave 3 upon treatment with 5% Pd-C at 100°. The structure of 7 was confirmed by its mass spectrum (peaks at m/e 368 and 325). Since alkyl radicals are very similar to hydrogen atoms in their rate of abstraction of hydrogen atoms from organic compounds and since hydrogen atoms abstract hydrogen from THF more than 150 times more readily than from t-butyl alcohol,[6] the intermediate trapped by addition of small amounts of t-butyl alcohol in our experiments must be the carbanion 2, as shown in Scheme I, rather than the corresponding free radical.

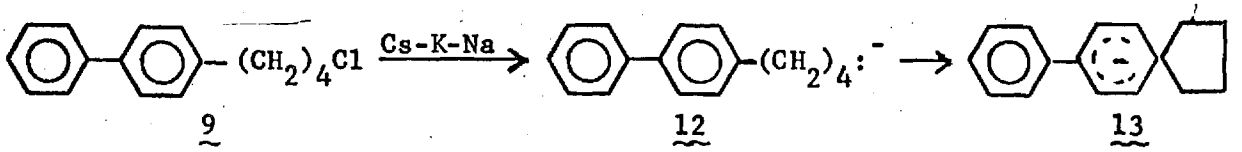
Reaction of the chloride 1 with potassium in the more acidic solvent dioxane at 101°, rather than THF at 65°, gave the rearranged hydrocarbon 6 (75% yield) and no detectable 3; however, repetition with sodium in place of potassium gave an 8 to 92 ratio of rearranged to non-rearranged hydrocarbons (6/3). These reactions in the solvent dioxane

confirm the conclusions derived from work in THF and show moreover that the rate of rearrangement of the organopotassium compound 2 greatly exceeds that of the corresponding organosodium compound. The inequality of rate between sodium and potassium compounds in carbanion rearrangements has not been previously observed although it has been known for some time that organolithium compounds rearrange more slowly than organosodium or organopotassium compounds.[7]

According to Scheme I the spiro anion 4 is an intermediate in the present carbanion rearrangement. In an attempt to detect this intermediate the chloride 1 was allowed to react with excess finely divided Cs-K-Na eutectic[1] in THF at -75° for some three minutes before carbonation. There was obtained, however, only the usual product of rearrangement, 5-p-biphenylyl-2,2-diphenylpentanoic acid. This result implies that the spiro anion 4 rearranges readily to 5 even at -75°. Since ready ring opening may be dependent upon the presence of the two phenyl groups which stabilize the final anion 5, this study has been repeated with the corresponding chloride 4-chloro-1-p-biphenylylbutane[2] (9) in which the activating phenyls have been replaced by hydrogen.

Reaction of 9 with excess Cs-K-Na eutectic at -70° in THF gave a red solution which was carbonated as soon (~ 4 min) as it started to turn green (radical anion formation). There was isolated a high yield of acid (ca. 85%) which consisted of 96% of 8-phenylspiro[4.5]-6,9-decadiene-8-carboxylic acid (10), mp 130-131°, and 4% of 2-p-biphenylylpentanoic acid (11). The analytical and spectral properties of 10 [λ_{max}^{EtOH} 260 nm (ϵ 293); nmr ($CDCl_3$) τ -1.40 (1 H, CO_2H), 2.80 (5 H, s),

4.00 (2 H, d, J = 10 Hz), 4.20 (2 H, d, J = 10 Hz), 8.33 (8 H, broad s); mass spectrum, molecular ion m/e 254] agree well with the assigned structure. Protonation of the red solution by methanol at -70° gave a neutral product of which only some 10% was volatile; the latter consisted of about equal amounts of 1-p-biphenylylbutane and 8-phenylspiro[4.5]-6,9-decadiene [nmr ($CDCl_3$) τ 2.75 (5 H, s), 4.33 (4 H, d, J = 1 Hz), 6.08 (1 H, t, J = 1 Hz), 8.27 (8 H, broad s)]. Reaction of 9 in THF with cesium at 35° or with cesium or potassium at 65° gave a similar mixture of carbanions although the yield of volatile products obtained upon carbonation decreased with increasing temperature. The nmr spectrum at 40° of the red solution from treatment of 9 with Cs-K-Na alloy in THF-d_8 at -70° and addition of mercury to remove excess alkali metal and destroy radical anion [τ 3.1-3.3 (5 H, m), 3.70 (2 H, d, J = 10 Hz), 5.60 (2 H, d, J = 10 Hz), 8.28 (4 H, m), 8.57 (4 H, m)] showed conclusively[8] that the major intermediate was the spiro anion 13. That the cyclization to



9 12 13

13 occurred via the open carbanion 12 was indicated by reaction of 9 with potassium in THF containing t-butyl alcohol wherein 1-p-biphenylylbutane was initially formed but was reduced ultimately to 1-(p-cyclohexylphenyl)butane. Since 4-p-biphenylyl-1-chlorobutane-1,1-d_2 gave 1-(p-cyclohexylphenyl)butane-4,4-d_2, cyclization did not occur prior to formation of the butane; also reaction of this chloride with sodium in dioxane at 101° gave 1-p-biphenylylbutane-4,4-d_2.

While species similar to 13 have been long suggested as intermediates or transition states[7b,9] in 1,2-migrations of aryl in polyarylethyllithiums, such carbanions have never previously been isolated from cyclization of ω-arylalkyl anions. A recent study[10] on "homoconjugation" in pyridylalkyl organometallic compounds indicated on the basis of nmr spectra that the compounds studied existed in the open chain form although attack by some electrophilic reagents gave spiro products. Similarly the reaction of the methiodide of 1-chloro-2-methyl-2-(4-pyridyl)propane with lithium in THF gave 1-methyl-4-(1,1-dimethylspirocyclopropyl)-1,4-dihydropyridine.[11]

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(2) All new compounds gave elemental analyses and nmr spectra consistent with the assigned structures.

(3) This reagent was prepared in ether by reaction of sodium amalgam with p-biphenylyldiphenylchloromethane [for the latter see N. N. Lichtin and H. Glazer, J. Amer. Chem. Soc., 73, 5537 (1951)].

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GEORGIA INSTITUTE OF TECHNOLOGY
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January 18, 1972

National Science Foundation
Washington, D. C. 20550

Attention: Office of the General Counsel

Subject: Possible Invention under Grant No. GP-19251

Gentlemen:

We recently submitted a renewal proposal (November 1, 1971) under the subject grant, Included with the proposal was a progress report prepared by the Principal Investigator, Dr. Erling Grovenstein, Jr., describing work performed during the period from May 1, 1970 through September 30, 1971. I have discussed this report with Dr. Grovenstein and he informs me that it is his opinion that certain of the work reported therein may be patentable. However, in this connection it should be noted that we have not conducted a preliminary patentability search or made an extensive review of the literature.

The work to which we refer relates to the "Reactions of Cesium and Cs-K-Na Alloy with Aromatic Hydrocarbons" and is set forth on pages A-15 through A-22 of the report. We have reproduced and enclose a copy of these pages for your information and file.

It should also be noted that the Georgia Institute of Technology feels that the best interests of the scientific community will be served by publication of this work rather than by the filing of a patent application. However, in the event NSF desires to file a patent application, we will be pleased to cooperate in all respects and to execute all required documents.

If we may be of further assistance concerning this matter, please let us know.

Very truly yours,

Milton W. Bennett
Assistant Director

MWB:ces
Enclosure: Pages A-15 to A-22 of Progress Report
cc: Dr. E. Grovenstein, Jr.